

IV. MICROSCOPIC REVERSIBILITY AND THE INFORMATION CONTAINED IN THE COMPOSITION VECTOR

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ABSTRACT

In equilibrium systems, transitions at microscopic level are reversible. In this work the microscopic level is defined as the one corresponding to such a detailed description of the system composition that the observer, (1) for inability, cannot give, or (2) for his own decision, does not give. (These two situations, for practical purposes, are equivalent.) In order to clarify this point, theoretical aspects underlying the physical approach to chemical equilibrium problems are examined. On one hand, the reduction of the composition vector dimension carried out with no loss of the information needed to identify the system, results in the existence of element potentials. On the other hand, the element potentials independence on the state of the particles is compatible with dynamics at microscopic level and makes the Thermodynamics formalization consistent with this experimental fact. Therefore, as during reversible processes no composition information is generated by the system, when transforming composition variables, microscopic reversibility is the other side of the coin.

***Key index phrases:* microscopic reversibility; dynamic equilibrium;**

Chemical Thermodynamics; amount of information; conservation of information

1. INTRODUCTION

This work introduces definitions for both *information* and *amount of information* which can be used to bring together the basis of the physical approach to chemical equilibrium problems and the concept of microscopic reversibility.

In part I (Luetich 2002a), the observer-dependency of the composition description was pointed out. In accord with this, here information will be a *difference which finds a difference*, i.e. a conceptual difference in the observer mind confirmed by something in the system (Qvortrup 1993). Thus, the amount of information will be the number of independent variables given by the composition vector.

This paper is the last one of a group of four related works written to give insight into the concept of *microscopic reversibility*. The aim here is to connect some basic concepts: equilibrium, homogeneity, levels of observation, amount of information, and reversibility.

2. A WEB OF CONCEPTS

EQUILIBRIUM AND COMPOSITION INFORMATION

For closed systems, transformed composition variables have the same value at non-equilibrium and stable states; but only in the latter ones the knowledge of the E components of \mathbf{n}^* is enough, since the remaining R components come from the constraints imposed by equilibrium (Luetich 2002a).

$$\mathbf{n}^* = \mathbf{C} \mathbf{n} \quad (2.1)$$

$$K_i = K_i(T, P, \mathbf{n}) \quad i = 1, \dots, R \quad (2.2)$$

Here, \mathbf{n} is the composition vector, \mathbf{C} is the transformation matrix, and K is the thermodynamic equilibrium constant.

Given the quantities of each element constituting the system, the quantity of each compound can be determined.

$$\text{information given by } \mathbf{n} \stackrel{\Delta}{=} \text{components of } \mathbf{n}^* \quad (2.3)$$

Vectors \mathbf{n} and \mathbf{n}^* give the same message.

The *amount of information* given by the composition vector can then be defined as the dimension (i.e. the number of components) of the corresponding element composition vector.

$$\text{amount of information given by } \mathbf{n} \stackrel{\Delta}{=} \text{dimension of } \mathbf{n}^* \quad (2.4)$$

[Differences between amount of information and the space occupied by information (codification) are shown in appendix A.]

The amount of information needed to identify the system given by \mathbf{n} and \mathbf{n}^* is the same. From now onwards, the equality in amounts of information will be indicated as follows:

$$\mathbf{n}^* \stackrel{i}{=} \mathbf{n}. \quad (2.5)$$

The description of stable states requires less variables than the description of unstable or non-equilibrium states. (From another point of view, systems in stable states give the minimum amount of information.) *Stable states are the ones which require the minimum number of composition variables.*

For non-equilibrium states, the number of particles of all present species must be consigned. In this case, the amount of information provided by a vector that only gives concentrations of some components is not enough.

Much information is equal to complexity, chaos, while "reduced" information, complexity reduction is equal to order. Order is created by erasing information, i.e. by reducing complexity (Qvortrup 1993). Equations like (2.2), give a structure to the system.

INFORMATION AND THE FUNDAMENTAL EQUATION

A fundamental equation provides the value of some thermodynamic function of a system, in each stable state \mathbf{m} .

According to condition (2.5),

$$(\mathbf{m}, \mathbf{n}^*) \stackrel{i}{=} (\mathbf{m}, \mathbf{n}). \quad (2.6)$$

As a consequence, for example,

$$G = G(T, P, \mathbf{n}^*). \quad (2.7)$$

That is to say, the fundamental equation can be written using the minimum number of composition variables (Luetich 2002a).

Variables T , P and \mathbf{n}^* can be chosen as the natural variables of function G because, for closed systems, the components of vector \mathbf{n}^* are independent variables. Thus, \mathbf{n}^* can be used as the name of the system.

INFORMATION AND LEGENDRE TRANSFORMATIONS

Assuming the convexity of the thermodynamic functions, the ones resulting from applying Legendre transformations to the fundamental equation have the same information (Tester & Modell 1997).

As regards to the states characterization, functions G and G^* contain the same information (Luetich 2002c).

$$G(T, P, \mathbf{n}) \stackrel{i}{=} G^*(T, P, \mu) \quad (2.8)$$

$$G(T, P, \mathbf{n}^*) \stackrel{i}{=} G^*(T, P, \zeta) \quad (2.9)$$

The importance of equation (2.8) should be found in the fact that the *state variables* T , P , and ζ are homogeneous in any system (multi-phase, multi-reaction). This is a consequence of the homogeneity of G with respect to \mathbf{n}^* (Luetich 2002a). Variables T , P , and ζ are the intensive factors which go with S , V , and \mathbf{n} , the capacity factors of each term of the Combined First and Second Law.

Taking into account equation (2.6),

$$\mu \stackrel{i}{=} \zeta. \quad (2.10)$$

The fact that we can assign the same property ζ to atoms in different states is a consequence of the atoms coupling with an equilibrium environment (von Oppen 1996).

HOMOGENEITY AND THE FUNDAMENTAL EQUATION

The Gibbs energy form of the fundamental equation is the function of the minimum values of the Gibbs energy of the system corresponding to each set of variables (T , P , \mathbf{n}^*). In equation (2.7),

$$G = \min G. \quad (2.11)$$

This condition can be divided into two others:

$$G = \mathbf{n}^T \boldsymbol{\mu}; \quad (2.12)$$

$$(dG)_{TP} = \boldsymbol{\mu}^T d\mathbf{n} = 0, \quad (2.13)$$

where $\boldsymbol{\mu}$ is the vector whose components are the chemical potentials.

This way of expressing the variation of G that corresponds to certain variation of \mathbf{n} is valid when function G is homogeneous with respect to \mathbf{n} (Euler theorem).

$$G(k\mathbf{n}) = k G(\mathbf{n}) \quad : k \in \mathbb{R} \quad (2.14)$$

The meaning to be assigned to the word *homogeneous* has been discussed when studying phases in equilibrium (Luetich 2002ac).

REVERSIBILITY AND COMPOSITION INFORMATION

The reason why stable states require the minimum number of variables is that these are unique, whereas non-equilibrium states are innumerable. As a consequence, the Second Law is an inequality for evolutions through non-equilibrium states (irreversible) and it is an equality for evolutions through stable states (reversible).

$$(dG)_{TP} > 0 \quad (\text{irreversible processes}) \quad (2.15)$$

$$(dG)_{TP} = 0 \quad (\text{reversible processes}) \quad (2.16)$$

In reversible evolutions of closed systems, the number of variables needed to describe the composition of the system and their values do not change. *The reversibility condition is the condition of conservation of the composition information.*

A closed system does not generate information when it evolves through stable states. It can be said that the fact of being unable to obtain information is the price we have to pay for making the system to evolve reversibly (i.e. for obtaining the maximum work).

The use of reversibility as the condition of conservation of information was illustrated by Margolus (1984) who modelled thermodynamic systems by means of cellular automata.

HOMOGENEITY AND LEGENDRE TRANSFORMATIONS

The complete Legendre transformation of equation (2.13) with respect to \mathbf{n} leads to the well-known Gibbs-Duhem equation.

$$\mathbf{n}^T d\mu = 0. \quad (2.17)$$

Although element compositions remain unaltered during a chemical reaction, by using the same procedure we obtain an analogous relationship among element potentials.

$$(\mathbf{n}^*)^T d\zeta = 0 \quad (2.18)$$

ζ is the vector whose components are the element potentials.

This conclusion is made since G^* is an homogeneous function of element composition variables (Luetich 2002c).

The condition for a system to evolve without changing the amount of information needed to define its composition is that the conjugate of composition variables change according to the condition:

$$(dG^*)_{TP} = -(\mathbf{n}^*)^T d\zeta = 0. \quad (2.19)$$

This is the thermodynamic definition of element composition variables.

It is important to note that equation (2.1) –the only mathematical (non-thermodynamic) equation here used– does not break the homogeneity condition since it is valid for any sufficiently large portion of the system.

REVERSIBILITY AND PSEUDOISOMERISATIONS

Elements are made up of particles having intrinsic differences, and not of equal particles in different states. Changes occur in the atoms environment, not in their nature (Luetich 2002a). States change; names do not (physical approach). Every reversible transitions are (pseudo)isomerisations.

HOMOGENEITY AND REVERSIBILITY

In stable states, the number of variables is the minimum because the entropy (disorder) is the maximum. Taking into account that one aspect of disorder is the disorganization of atoms, it is easy to see that the major disorder implies a greater homogeneity. This is another way of considering the relationship among the homogeneity idea, the reversibility concept, and the Second Law. (Note that the same thing happens when we assign to the thermal state of a system only *one* variable (the temperature); this could not be done if the state was not homogeneous.)

The definitions introduced above are in agreement with Wiener's point of view of the concept of information. The following paragraph was taken from his book *Cybernetics* (1948):

The notion of the amount of information attaches itself very naturally to a classical notion in statistical mechanics: that of entropy. Just as the amount of information in a system is a measure of its degree of organisation, so the entropy of a system is a measure of its degree of disorganisation.

Therefore, the fact that stable states can be described with the lowest number of composition variables and the fact that the potential defining these states is homogeneous with respect to these variables are closely related. However, it is possible to think of (hypothetical) non-equilibrium homogeneous states, like the ideal gas state. All stable states are homogeneous, as indicated by equation (2.13), but not all homogeneous states can be identified by means of the element composition vector.

SUMMARY

Two ideas constituted the main thread of the reasoning made throughout the three previous works (Luetich 2002abc): amount of information and homogeneity. In this work, the existing relationship between them has been shown.

Among all the settled relationships, from here on emphasis will be placed on the one existing between reversibility and conservation of information. The aim is to

demonstrate that just as in reversible transitions information is kept, the observer must assume that non-observable inter-conversions are reversible.

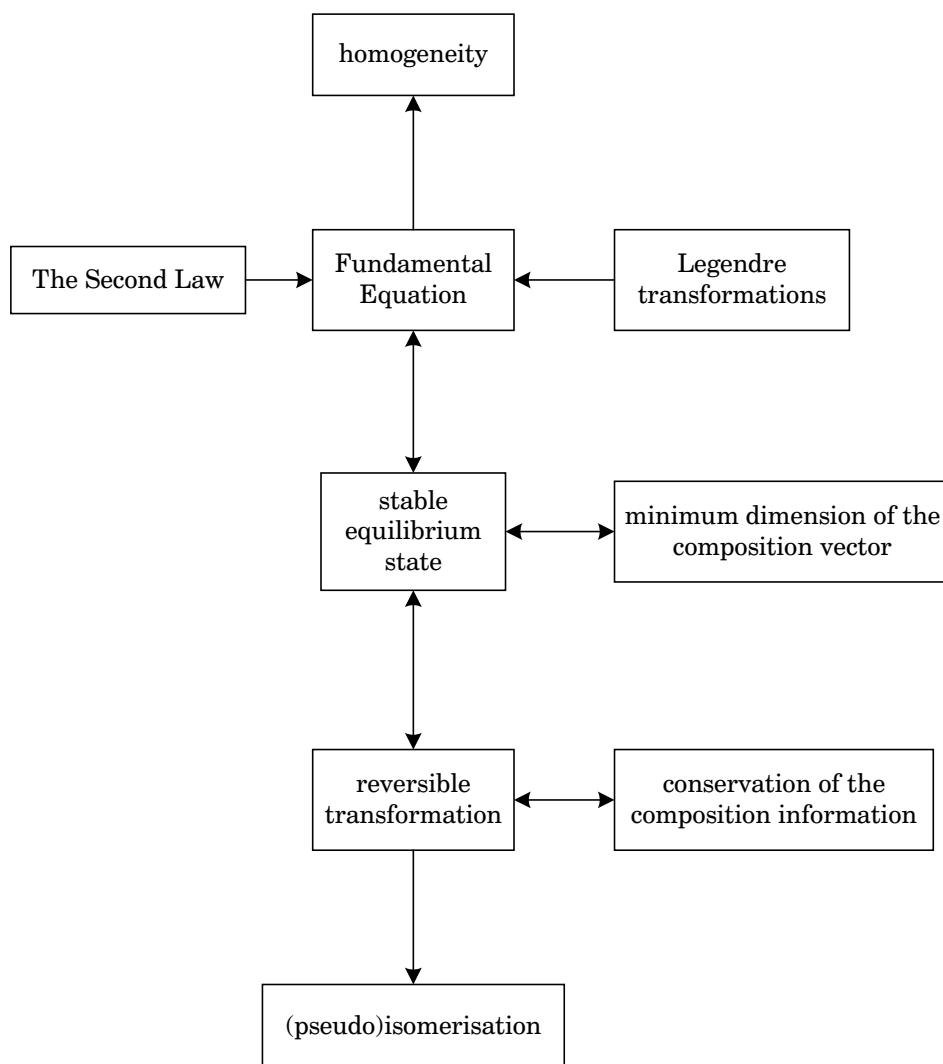


Figure 1

Interdependence of some basic concepts of Chemical Thermodynamics:
homogeneity, reversibility, information conservation

Figure 1 presents a diagram showing the interdependence of the aforementioned concepts. These relationships are of interest for a wide group of fields, including the theory of computational modelling of physics-like systems (Margolus 2001).

3. REVERSIBILITY AT THE MICROSCOPIC LEVEL

DETAILED MASS BALANCE

A system in physico-chemical equilibrium can be considered as a special case of a kinetic system in which the variations with time of all the concentrations are null.

Under these conditions, the principle of detailed balance must be fulfilled: *For systems at equilibrium, any microscopic process and its inverse occur on average at the same time.* (This is a variant of the statement introduced by Tolman in 1938.)

MICROSCOPIC REVERSIBILITY

Appendix B suggests that the equality of element potentials for particles of the same class in different states is due to the fact that the interconversion between potential and movement energies at the microscopic level does not imply a change in the system capacity for performing work. This conclusion is valid for all transitions studied by Chemical Thermodynamics (physical and chemical transitions), since the principle of detailed balance is fulfilled by all of them.

It should be noted that there exists a close conceptual relationship between microscopic reversibility and detailed balance, which has led some authors to use these expressions as synonyms.

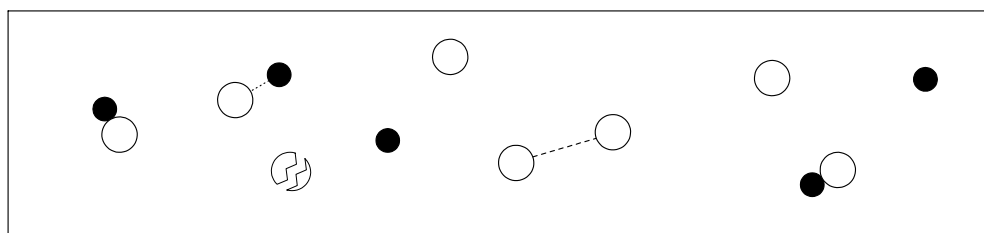
STATES AT THE MICROSCOPIC LEVEL

Particles of the same class can be distinguished by their state. Different physical aggregation states can be easily recognized by observation. By means of analysis, chemical aggregation states can be determined. These states belong to the macroscopic level of description.

At a deeper level, different states cannot be distinguished due to our limited senses and our also limited observation instruments; but it can be conjectured that particles are in different states. This is the microscopic level of description.

Figure 2 shows the representation of a phase containing three species in equilibrium: $A+B \rightleftharpoons C$. By chemical analyses we can determine the quantities of

free A and B and the quantity of combined A and B. However, it is impossible to directly measure how many particles are, for instance, in the A-B transition aggregation state. The potential assigned to these particles is the same because they cannot be distinguished: the association that leads to the transition complex formation and then to a more stable aggregate must be reversible. The same reasoning can be applied to the associated particles –for example, by means of H-bridges (A---A)– or the dissociated ones (2 A/2).



(i)

	Chemical Kinetics	stoichiometric formulation	nonstoichiometric formulation
macroscopic level			
microscopic level			

(ii)

Figure 2

Description of the composition of the system A-B-C=AB

(i) exhaustive: free A (○); associated A (○---○); dissociated A (2 ○/2); free B (●);
transition complex (○---●); compound C (○●)

(ii) when attention is focused on components and transition aggregates; according to an observer who distinguishes components (stoichiometric formulation); according to an observer who distinguishes elements (physical approach)

Within the physical approach to chemical equilibrium problems (Luetich 2002a) composition variables are transformed according to:

$$\begin{cases} n_A^* = n_A^{A/2} + n_A^{\text{free}} + n_A^{A---A} + n_A^{A-B} + n_A^{AB} \\ n_B^* = n_B^{\text{free}} + n_B^{A-B} + n_B^{AB} \end{cases} \quad (3.1)$$

where n_i^* is the number of the i -th element atoms in any state; n_i^{free} is the number of free atoms; n_i^{i-i} is the number of self-associated atoms; n_i^{i-j} is the number of atoms in the transition complex; n_i^{AB} is the number of atoms in

molecule AB; and $n_A^{A/2}$ is the number of "dissociated atoms" of A, i.e. $1/2 n^{A/2}$. (Atoms are the smallest piece in which we *arbitrary* divide an element.)

In the stoichiometric formulation composition variables are transformed according to:

$$\begin{cases} n_A^* = n_A^{A/2} + n_A^{\text{free}} + n_A^{A\text{---}A} + n_A^{A\text{--}B} \\ n_B^* = n_B^{\text{free}} + n_B^{A\text{--}B} \\ n_C^* = n_C^{\text{free}} \end{cases} \quad (3.2)$$

In Chemical Kinetics, attention is focused on components and intermediate aggregates. The transformation is:

$$\begin{cases} n_A^* = n_A^{A/2} + n_A^{\text{free}} + n_A^{A\text{---}A} \\ n_B^* = n_B^{\text{free}} \\ n_C^* = n_C^{\text{free}} \\ n_{A\text{--}B}^* = n_{A\text{--}B}^{\text{free}} \end{cases} \quad (3.3)$$

By means of measurement or calculus, species can be quantified, i.e. brought to the macroscopic level (the level of the observer). "Atoms" are those particles whose dissociation belongs to the microscopic level.

MICROSCOPIC REVERSIBILITY AND THE PHYSICAL APPROACH

Figure 3 shows the two levels of description. When the line that settles the limit between them is crossed, the direction of the implication in the remarked expression changes. When we detect different states but we do not note net changes, we say that there is equilibrium. When we cannot distinguish states, but we surmise they exist, reversible inter-conversions should be assumed, so that information does not change. Equilibrium is the cement when building a single particle with two particles which are not physically together, and when giving the same name to particles in different states.

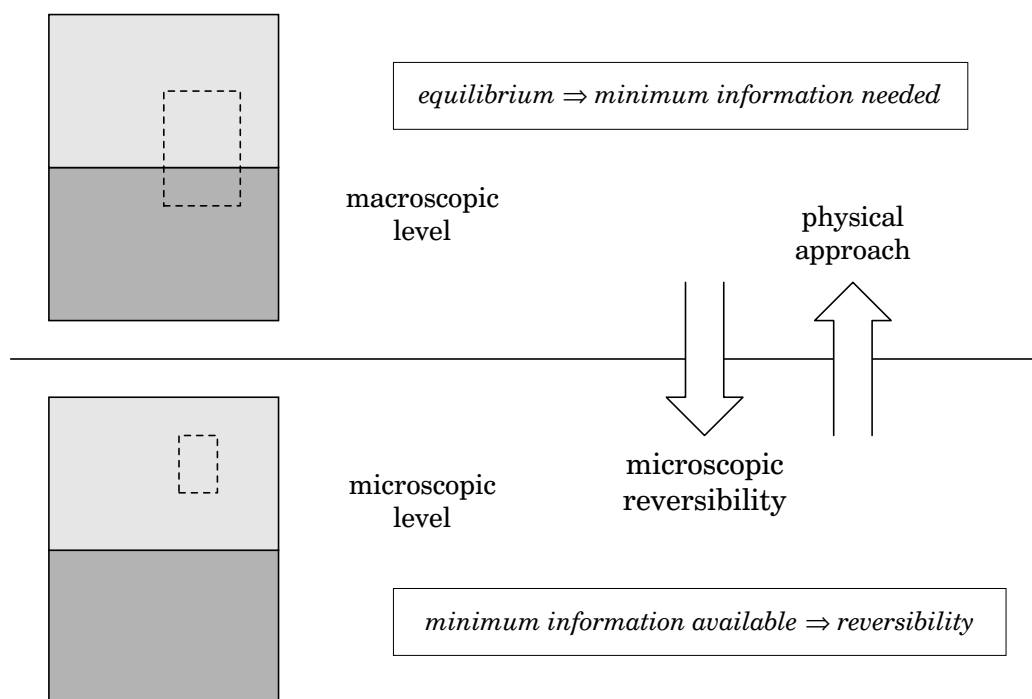


Figure 3

When crossing the limit that separates the macroscopic from the microscopic level, the direction of implication "equilibrium \Rightarrow minimum amount of information" is inverted

Note the importance of the observer's characteristics in this argumentation, which was stressed when studying the physical approach (Luetich 2002a). The fact that the observer sometimes *decides* to see or not certain states, demonstrates that not only his characteristics are important but also his role.

The difference between the human observer, who is always at the macroscopic level, and an imaginary entity as the *Maxwell's daemon* is that the latter distinguishes microscopic states.

4. CONCLUSIONS

The reduction of the dimension of the composition vector carried out with no loss of the information needed to identify the system results in the existence of element potentials. Thus, for systems at equilibrium, element potentials are not dependent on the state of the atoms (Luetich 2002c). This property makes the Thermodynamics formalization consistent with dynamics at microscopic level.

Contrariwise, when no new information comes from a system undergoing physico-chemical transitions, reversibility should be assumed. The principle of microscopic reversibility can be enunciated as follows: *processes at microscopic level are reversible*. This statement is useful when we agree what *microscopic*

means. In this work, the microscopic level was defined as that level corresponding to such a detailed description of the system composition which the observer does not give (1) for inability, or (2) for his own decision. This point of view leads to conclusions in agreement with the etymology of the words *microscopic* (from Greek μικρόν=*micrón*, "little" –in extension or importance– and σκοπέω=*scopéoo*, "watch", "recognise", "pay attention to") and *information* (from Latin *informāre*, "give form to").

Being the amount of information the number of its independent variables of the composition vector, stable states are the states which require the minimum amount of information. In such states (homogeneous), entropy reach its maximum value. As a consequence, in reversible evolutions, systems do not generate information.

There is a connection between the equality of element potentials in any system at equilibrium and the principle of microscopic reversibility. Such connection must be searched in our limitations to make a description at microscopic level of the stable system composition: variations produced by direct and inverse microscopic processes in macroscopic variables are null; thus, we cannot give a detailed description of the composition.

The reason not to give a complete description may also be the observer's *deliberate myopia*. By means of powerful analytic instruments or by means of certain calculations –like in Chemical Kinetics–, some species can be brought to the macroscopic level. These new species, at a lower level, were in equilibrium with those considered in the stoichimetric formulation: they receive the same name. Inversely –like in any statistical approach, such as Molecular Kinetics–, we can define *mean* entities to *represent* sets of particles of different masses and in different states (position, velocity). The unique molecular process is then reversible.

The macroscopic and microscopic levels of description of the composition of stable systems are coupled because of the equivalence:

$$\textit{equilibrium} \Leftrightarrow \textit{minimum information}, \quad (2.1)$$

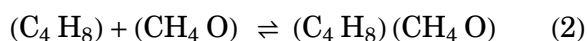
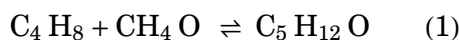
illustrated in figure 3.

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APPENDIX A**THE INFORMATION CONTAINED IN THE COMPOSITION VECTOR:
AMOUNT AND CODIFICATION**

Here, the example of the reaction of adding methanol to isobutene (Luetich 2002a) will be re-considered.



The matrix **C** for expression (2), **C**₂, contains the same amount of information than the matrix **C** for expression (1), **C**₁. For stable states, another matrix indicating the amount of true element in each "element" exist.

Using a sort of basic algebra in tables (matrices), we can find out which is this matrix (**D**) and which is the operation that relates **C**₁ and **C**₂.

$$\frac{\text{atoms}}{\text{"atom"}} \frac{\text{"atoms"}}{\text{molecule}} = \frac{\text{atoms}}{\text{molecule}}$$

$$\left(\begin{array}{c|c} & \begin{pmatrix} 1 & 0 & 1 \\ 0 & 1 & 1 \end{pmatrix} \\ \hline \begin{pmatrix} 4 & 1 \\ 8 & 4 \\ 0 & 1 \end{pmatrix} & \begin{pmatrix} 4 & 1 & 5 \\ 8 & 4 & 12 \\ 0 & 1 & 1 \end{pmatrix} \end{array} \right)$$

It is apparent that

$$\mathbf{D} \mathbf{C}_2 = \mathbf{C}_1$$

where **D** is the matrix that gives the number of atoms of the true element in each "atom" of the "element".

In vector **n**^{*}, information contained in **n** has been expressed with a reduced number of variables. These new variables are more easy to interpret: we don't need to know anything about Chemistry. As Pérez Cisneros *et al.* (1997) have shown, if the elements are cleverly chosen, the reduction in the number of variables may simultaneously lead to (i) an easier graphical representation of the changes in the system composition, and (ii) new definitions based on the new variables. Thus, these authors defined the *element azeotropes* which appears when the element compositions of liquid and vapour at equilibrium coincide.

On the contrary, codification is an artificial reduction in the number of variables that complicates their interpretation. Let's say that quantity and complexity are inversely proportional. If the object was to reduce the number of variables to its minimum value

–thus taking interpretation to the maximum complication degree– we could resort to an extreme procedure. Composition variables are not real numbers. (The great size of the Avogadro's number makes us not to take this fact into account.) In this way, we could employ the codification method introduced by Gödel (1931): each atom is assigned a prime number, for example: 2 for carbon, 3 for hydrogen, and 5 for oxygen; the numbers of particles are then used as the exponents of each of them. If results are multiplied, they give a unique number for each composition that can be "decodified" decomposing it into prime factors.

$$2^{N_C} 3^{N_H} 5^{N_O}$$

The complication in interpreting variables would be observed in the chaotic behaviour of any thermodynamic property represented in a Cartesian diagram with respect to this variable (Luetich 1999).

APPENDIX B

DYNAMICS AT THE MICROSCOPIC LEVEL

Experiments with "marked atoms" in which phases or species in equilibrium get in contact –one of them with isotopic variants that the other one has in a too small quantity– show that, after some time, both are "contaminated". Variations –virtual at first– of N of the Third Theorem (Luetich 2002c) make Thermodynamics formalization consistent with these observations. In this appendix, another justification will be presented, describing systems at microscopic level.

ATOMS ENVIRONMENT IN PHYSICAL AND CHEMICAL EQUILIBRIA

The two basic differences between physical and chemical transitions are: (1) in physical transitions, there is a separation surface between both forms; in chemical transitions, both are mixed; and (2) in the latter, both forms receive different names; the formers are only state changes.

Comparing liquid-vapour transitions with isomerisations in the physical approach (Luetich 2002a), we see that difference (2) does not exist. As regards (1), if the inter-phase region is not too large, it matches the mixing free energy.

In any case, the equilibrium condition is the equality of element potentials (partial molar Gibbs energies) for all particles of the element –and not the equality of molar Gibbs potentials–. But if a mol of the element was an insignificant quantity for the system (big system), for practical purposes, the element potential in the mixture is the change in its Gibbs energy that would be produced by introducing a mol in the mixture: the molar property and the partial molar property would coincide.

$$\mathbf{n} \rightarrow \infty \Rightarrow \bar{G}_i = \left(\frac{\partial G}{\partial n_i} \right)_{\mathbf{n}[i]} = \left(\frac{\Delta G}{\Delta n_i} \right)_{\mathbf{n}[i]} = \underline{G}_i$$

Dynamics at the microscopic level does not modify the system composition. Therefore, the effect produced by the system on each particle does not change. In other words, mixing effects can be neglected when dealing with few particles.

ENERGY AT THE MICROSCOPIC LEVEL

Here the following usual definition will be employed: «Energy is what can be transformed into work.» This definition includes both the movement energy (kinetic) –in any of its forms (translational, rotational, vibratory)– and the energy stored or not manifested as movement (potential) –in any of its forms (gravitational, electric, elastic, chemical)–.

If we take into account that the free energy of a process is the maximum amount of energy to be transformed into work and that according to what has been pointed out above, the mixing effect is null for transformations at microscopic level, the previous conclusions can be transferred to this case: the Gibbs potential of a particle (the chemical potential per particle of the Second Theorem) does not change when particles are associated, since this process is merely a change in the energy form.

Otherwise, if the entropic effect is null, S is constant and, as T and P are constant, E is also constant.

Physical equilibrium between a liquid phase and its vapour is interesting due to the analogies that can be made when studying chemical transformations (Luetich 2001). The molecules in a saturated vapour phase come near when entering the liquid phase. Equilibrium requires that other molecules in the liquid phase simultaneously dissociate from one another and enter the vapour. In this way, the principle of conservation of energy is fulfilled: if the kinetic energy (mostly translational) of molecules in the vapour phase is transformed into potential (electric) when they go to the liquid phase, and the opposite occurs in the inverse process, there are neither losses nor gains. Particles move as a mass directed to compress a spring: the deformation of the electronic cloud is equivalent to the deformation of the spring.

REFERENCES

- Gödel, K. 1931 Ueber formal unentscheidbare Sätze der Principia Mathematica und verwandter Systeme. I. *Monatsh. Math. Physik* **38**, 178-198.
- Luetich, J. J. 1999 *The choice of variables to define the composition of systems in chemical equilibrium*. Proceedings to the 3rd Meeting of Young Researchers, UNL, Santa Fe, Argentina.
- Luetich, J. J. 2001 *Five Contributions to Reactive Distillation Thermodynamics*. PhD thesis, Universidad Nacional del Litoral, Santa Fe, Argentina.
- Luetich, J. J. 2002a I. The Gibbs energy form of the fundamental equation for multi-phase multi-reaction closed systems within the physical approach. *Trans. Luv. Acad.* **1**, 1-23.
- Luetich, J. J. 2002b II. Linear combinations, Lagrange multipliers and Legendre transforms—a look at three methods to write the Gibbs energy of reactive mixtures. *Trans. Luv. Acad.* **1**, 25-39.
- Luetich, J. J. 2002c III. Three fundamental theorems on chemical Thermodynamics. *Trans. Luv. Acad.* **1**, 41-55.
- Margolus, N. H. 1984 Physics-like models for computation. *Physica* 10D, 81-95.
- Margolus, N. H. 2001 A bridge of bits. <http://www.im.lcs.mit.edu/poc/margolus>.
- Oppen, G. 1996 Objects and environment. *Physics–Uspekhi* **39**, 6, 617-622.
- Qvortrup, L. 1993 The controversy over the concept of information. *Cybernetics & Human Knowing* **1**, 4.
- Tester, J. W. & M. Modell 1997 *Thermodynamics and Its Applications*, 3rd edn, pp. 142-162. New Jersey: Prentice Hall.
- Tolman, R. C. 1938 *The Principles of Statistical Mechanics*. London: Oxford University Press.
- Wiener, N. 1948 *Cybernetics*, p. 18. MIT Press.