

III. THREE FUNDAMENTAL THEOREMS ON CHEMICAL THERMODYNAMICS

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ABSTRACT

Chemical Thermodynamics is the unified theory of physical and chemical transitions. This work presents three theorems on which the whole subject can be grounded. The first of them reveals the existing connection between the Lagrange multipliers method of the non-stoichiometric formulation and the homogeneity condition which is implicit in most of thermodynamic equations. However, this condition is less restrictive than the homogeneity of the system, i.e. of all its properties; it solely deals with the Gibbs energy homogeneity with respect to the composition vector. Thus, equations can also be applied to equilibrium multi-phase systems. The second one looks into the element definition used in the physical approach to chemical equilibrium problems: element potentials do not depend on the particles state because the Gibbs energy is an homogeneous function of the element composition vector. The third one shows the relationship between the definition of element potential and the dynamics of equilibrium at the microscopic level: this definition corresponds to a change in the element particles number in any state—element potentials are homogeneous magnitudes of zeroth degree. These three theorems are different ways to present the same idea: the concept of homogeneity and its consequences.

***Key index phrases:* Gibbs energy; Chemical Thermodynamics; Lagrange multipliers; Legendre transformations; dynamic equilibrium**

Received on the 7 th August 2001

Trans. Luv. Acad. 2002, **1**, 37 -50

ISSN 1666 -7581

Accepted on the 19 th December 2001

[ftp.luventicus.org/papers/02_TLA001iii.pdf](ftp://luventicus.org/papers/02_TLA001iii.pdf)

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1. INTRODUCTION

Gibbs' success in solving the problem of energetics in phase changes led to transferring his conclusions to chemical transitions, giving rise to Chemical Thermodynamics.

In physical transitions, both forms (states) of a substance are separate by a surface. In chemical transitions, both forms are mixed. The sole difference between a phase change of a pure body and an homogeneous isomerisation lies on the mixing free energy. In the case of a vapour-liquid transition, equilibrium is possible because the particles energy, which is mostly kinetic in the vapour state, is mostly potential in the liquid state. In the case of an isomerisation, the coexistence of both forms is due to the stabilization produced by the mixture, associated to an always negative free energy.

These differences do not prevent the development of a common formalization for all these transitions. This is possible working with partial molar properties: the mixing effect corresponding to differential changes in composition is null. Therefore, the condition of equality of the Gibbs energy changes associated to differential changes of the element mass (μ) is the equilibrium condition for any physical or chemical transition.

In this work, we will look into the root reasons for unifying the study of all transitions. For this purpose, it will be demonstrated that the homogeneity condition of the Gibbs energy with respect to the composition vector is responsible for the existence of element potentials (multipliers) (First Theorem). The existence of such potentials brings down the barrier that separates physical from chemical transitions, i.e. the change in names which goes with the latter ones. On the basis of this conclusion, it is possible to assign a change in names to vapour-liquid transitions or not to do it in the case of isomerisations (Second Theorem). Equality of partial molar properties μ have the implicit idea of dynamics at microscopic level, which is shown by means of experiments (Third Theorem).

The First Theorem reveals the connection existing between the traditional, non-stoichiometric formulation of chemical equilibrium problems (Smith & Missen 1991) and a variant of the method introduced by Alberty (1997) to obtain the expression of element potentials. The Second Theorem shows the independence of potentials on states, and it is a generalization of the statement

given by Beattie & Oppenheim (1979). The Third Theorem highlights the essentially dynamic aspect of element potentials definition (Gerasimov 1971).

The three statements are conceptually closed related, so they are presented together and in the mentioned order. They can serve as foundation for the whole Chemical Thermodynamics (Luetich 2001).

This work is the third of a group of four related works written to clarify the physical sense of the idea of *microscopic reversibility*. The emphasis here is laid on the concepts of homogeneity and dynamics at the microscopic level.

2. STATEMENTS AND DISCUSSIONS

FIRST THEOREM

LINEAR MINIMIZATION AND THE HOMOGENEITY CONDITION

When the objective function of the Lagrange multipliers method is a homogeneous function with respect to the variables subject to constraints, the auxiliary function (Lagrangian) is the complete Legendre transform of the objective function with respect to the same variables. The auxiliary function and the objective function contain the same information.

HYPOTHESES

a. Let the function

$$G = G(\mathbf{m}, \mathbf{n}) \quad (2.1)$$

be homogeneous with respect to \mathbf{n} , i.e.,

$$G(\mathbf{m}, k \mathbf{n}) = k G(\mathbf{m}, \mathbf{n}) \quad : k \in \mathbb{R}. \quad (2.2)$$

Otherwise,

$$G = \sum_{i=1}^C n_i \mu_i, \quad (2.3)$$

being n_i the components of \mathbf{n} , and C the dimension of \mathbf{n} .

b. There is a matrix $\mathbf{C} = \mathbf{C}_{E \times C}$, so that

$$n_j^* = \sum_{i=1}^C c_{ij} n_i, \quad j = 1, \dots, E < C, \quad (2.4)$$

where c_{ij} is the component of \mathbf{C} corresponding to line i and column j , and E the dimension of \mathbf{n}^* .

DEMONSTRATION

According to hypotheses a and b , G could be written in a more compact way:

$$G = \sum_{j=1}^E n_j^* \zeta_j, \quad (2.5)$$

where ζ_j are linear combinations of μ_i .

Defining the transformed function

$$G^* \triangleq G - \sum_{j=1}^E n_j^* \zeta_j, \quad (2.6)$$

we have

$$\sum_{i=1}^C n_i \mu_i - \sum_{j=1}^E n_j^* \zeta_j = G^*. \quad (2.7)$$

Then, substituting the variables n_j^* , we obtain

$$\sum_{i=1}^C n_i \mu_i - \sum_{j=1}^E \sum_{i=1}^C c_{ij} n_i \zeta_j = G^*. \quad (2.8)$$

In a more practical way,

$$\sum_{i=1}^C \left(\mu_i - \sum_{j=1}^E c_{ij} \zeta_j \right) n_i = G^*, \quad (2.9)$$

and, giving a name to the first factor of the sum,

$$\sum_{i=1}^C \mu_i^* n_i = G^*. \quad (2.10)$$

For this equality to be always achieved when $G^* = 0$,

$$\mu_i^* = 0, \quad (2.11)$$

and we finally deduce that

$$\mu_i - \sum_{j=1}^E c_{ij} \zeta_j = 0, \quad i = 1, \dots, C, \quad (2.12)$$

expressions from which ζ_i can be obtained.

According to hypothesis *a*,

$$dG = \sum_{k=1}^S \frac{\partial G}{\partial m_k} dm_k + \sum_{i=1}^C \mu_i dn_i, \quad (2.13)$$

where S is the dimension of \mathbf{m} , and

$$(dG)_{\mathbf{m}} = \sum_{i=1}^C \mu_i dn_i. \quad (2.14)$$

From equation (2.6),

$$(dG^*)_{\mathbf{m}} = \left[dG - \sum_{j=1}^E \sum_{i=1}^C (\zeta_j d(c_{ij} n_i) + c_{ij} n_i d\zeta_j) \right]_{\mathbf{m}}; \quad (2.15)$$

$$\left(\frac{\partial G^*}{\partial n_i} \right)_{\mathbf{mn}[i]} = \mu_i - \sum_{j=1}^E \sum_{i=1}^C \left(\zeta_j \frac{\partial(c_{ij} n_i)}{\partial n_i} + c_{ij} n_i \frac{\partial \zeta_j}{\partial n_i} \right)_{\mathbf{mn}[i]},$$

$$i = 1, \dots, C. \quad (2.16)$$

This equation is equivalent to equation (2.12), since the left-hand side is zero and the second term of the sum is null.

When $G^* \equiv 0$,

$$(dG^*)_{\mathbf{m}} = 0. \quad (2.17)$$

Therefore,

$$(dG^*)_{\mathbf{m}} = - \sum_{j=1}^E n_j^* d\zeta_j. \quad (2.18)$$

Thus, on the one hand, according to equations (2.5) and (2.18), and definition (2.6), G^* is the complete Legendre transform of G with respect to the components of \mathbf{n}^* ; and, on the other hand, according to the same definition, G^* can be viewed as the Lagrange auxiliary function (Lagrangian) for the optimization of G subject to conditions (2.4): ζ_j are the "multipliers".

COMMENTS

In the Lagrange multipliers method, variations of G are linear combinations of the variations of the components of \mathbf{n} . This is the same reason why we say that G is homogeneous of first order with respect to \mathbf{n} (figure 1): linearity and homogeneity are equivalent properties.

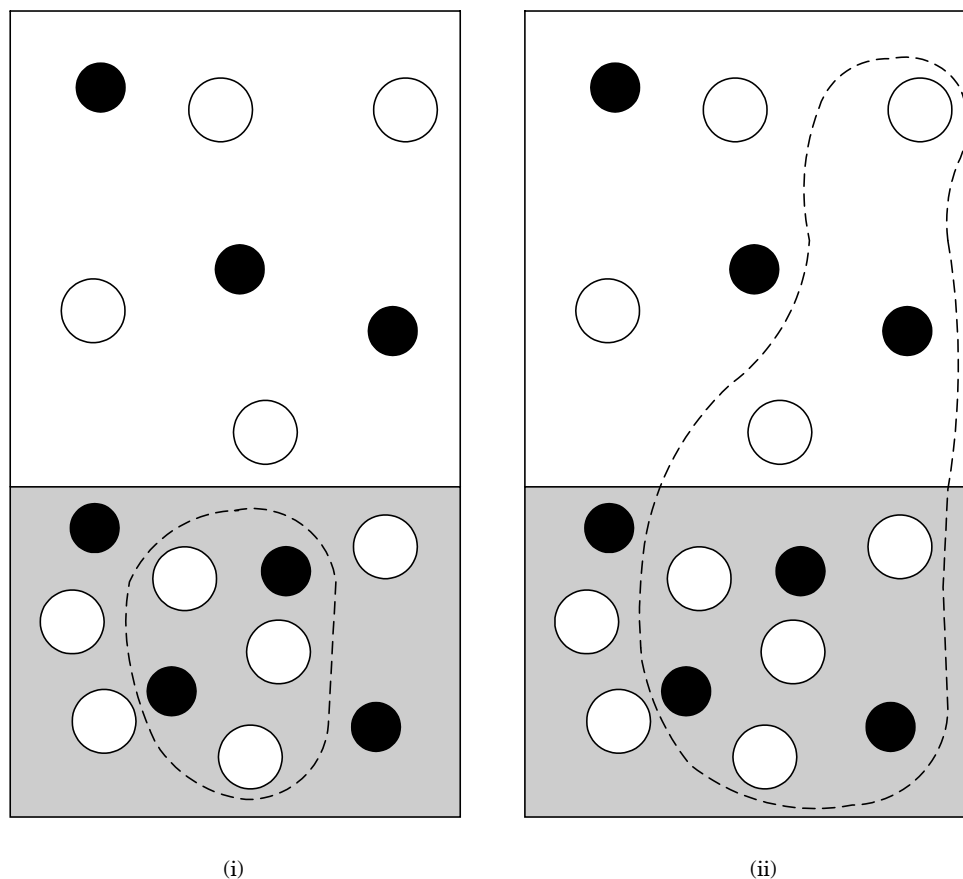


Figure 1

Illustration of the homogeneity of G with respect to \mathbf{n} in a vapour-liquid binary system

For the contained region: (i) $G(\mathbf{n}_1)$ and (ii) $G(\lambda\mathbf{n}_1) = \lambda G(\mathbf{n}_1)$. (Here, $\lambda = 2$.)

(G is not homogeneous with respect to V)

Therefore, when the complete Legendre transformation of a function to which the Euler theorem conclusions can be applied (homogeneous function) is performed, the results coincide with those obtained using Lagrange multipliers.

The Lagrange auxiliary function can be identified to the complete Legendre transform of the function G with respect to the components of \mathbf{n}^* (Luetich 2002b). Note that the Lagrangian

$$\Phi = \Phi(\mathbf{n}, \zeta), \quad (2.19)$$

and the complete Legendre transform $G(\mathbf{m}, \mathbf{n})$ with respect to \mathbf{n} is

$$G^* = G^*(\mathbf{m}, \boldsymbol{\mu}), \quad (2.20)$$

but as \mathbf{m} remains unchanged and the Legendre transformation is done with respect to \mathbf{n}^*

$$G^* = G^*(\mathbf{m}, \boldsymbol{\zeta}) = G^*(\boldsymbol{\zeta}) = G^*(\mathbf{n}^*, \boldsymbol{\zeta}). \quad (2.21)$$

The functions in pairs $\{G(\mathbf{m}, \mathbf{n}), G^*(\mathbf{m}, \boldsymbol{\mu})\}$ and $\{G^*(\mathbf{m}, \boldsymbol{\zeta}), G(\mathbf{m}, \mathbf{n}^*)\}$ contain the same information because each of them is the complete Legendre transform of the other with respect of the second variable. To connect these two sets and show that $G(\mathbf{m}, \mathbf{n})$ contains the same information as $G(\mathbf{m}, \mathbf{n}^*)$, this theorem shows that $G^*(\mathbf{m}, \boldsymbol{\zeta})$ contains the same information as $G(\mathbf{m}, \mathbf{n})$. This "diagonal" demonstration (figure 2) shows the equivalence of the non-stoichiometric formulation using Lagrange multipliers and the Chemical Thermodynamics formalization resorting to Legendre transformations.

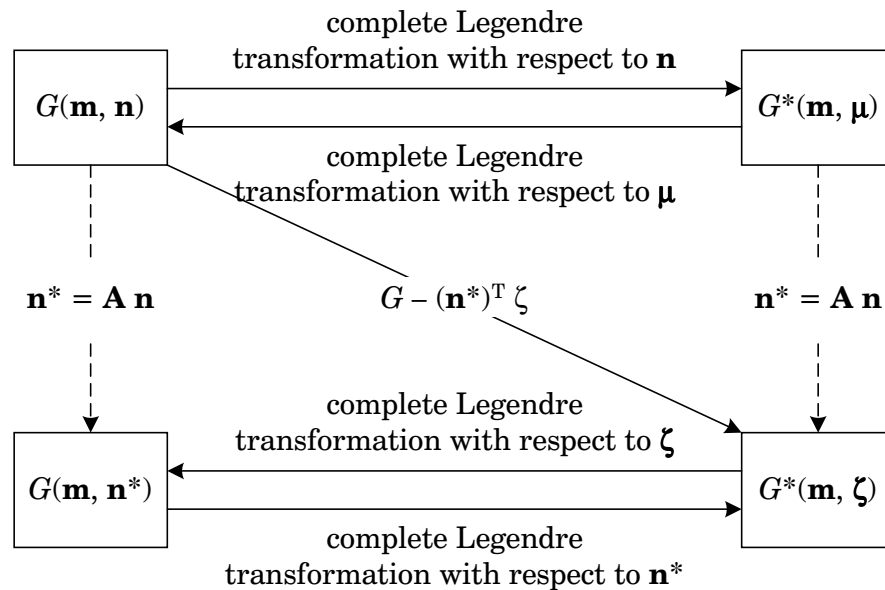


Figure 2

Diagonal demonstration of the equivalence of $G(\mathbf{m}, \mathbf{n})$ and $G(\mathbf{m}, \mathbf{n}^*)$

SECOND THEOREM

ELEMENT COMPOSITION VARIABLES AND ELEMENT POTENTIALS

For systems at equilibrium, the potential calculated for a particle is independent of its environment.

HYPOTHESIS

Let a system be at thermal, mechanic and chemical equilibrium; and α be certain aggregation state of the j -th element particles.

DEMONSTRATION

Going back to equation (2.5) and taking into account that transformed variables include the particles in their various states, we obtain

$$n_j^* = n_j^\alpha + \sum_{\varphi} n_j^\varphi, \quad (2.22)$$

separating the part corresponding to state α from the other ones (φ) (figure 3).

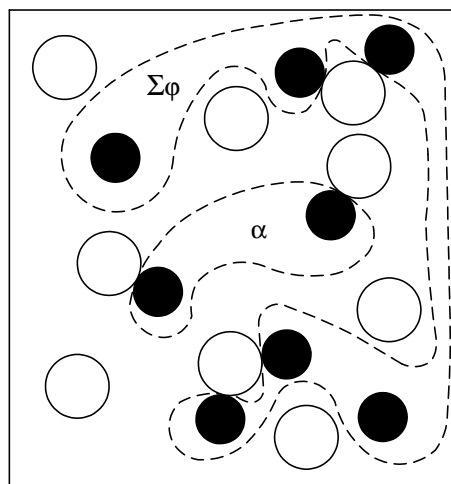


Figure 3

α and the other states ($\Sigma\varphi$) of element A(●) in the homogeneous two-element system A-B-AB-A₂B

The Gibbs energy of each species is the sum of the Gibbs energies of the species in each state.

$$G_j = G_j^\alpha + \sum_{\varphi} G_j^\varphi \quad (2.23)$$

The Gibbs energy of the whole system is the sum of the Gibbs energies of each state.

$$G = \sum_{j=1}^E G_j = G^\alpha + \sum_{\varphi} G^\varphi \quad (2.24)$$

The variation of the Gibbs energy with the number of particles of element j in the state of aggregation α is:

$$\left(\frac{\partial G}{\partial n_j^\alpha}\right)_{TP\mathbf{n}_{e[j]}^{\varphi[\alpha]}} = \left(\frac{\partial G^\alpha}{\partial n_j^\alpha}\right)_{TP\mathbf{n}_{e[j]}^{\varphi[\alpha]}} + \left(\frac{\partial \sum_{\varphi} G^\varphi}{\partial n_j^\alpha}\right)_{TP\mathbf{n}_{e[j]}^{\varphi[\alpha]}} = \left(\frac{\partial G^\alpha}{\partial n_j^\alpha}\right)_{TP\mathbf{n}_{e[j]}^{\varphi[\alpha]}}, \quad (2.25)$$

where $\mathbf{n}_{e[j]}^{\varphi[\alpha]}$ is the set of composition variables, except for the one for state α of element j .

Superscript α can represent any aggregation state, i.e.

$$\mu_j^\alpha = \left(\frac{\partial G^\alpha}{\partial n_j^\alpha}\right)_{TP\mathbf{n}_{e[j]}^{\varphi[\alpha]}} = \left(\frac{\partial G}{\partial n_j^\alpha}\right)_{TP\mathbf{n}_{e[j]}^{\varphi[\alpha]}} = \left(\frac{\partial G}{\partial n_j}\right)_{TP\mathbf{n}[j]} = \mu_j. \quad (2.26)$$

This property leads to the definition of the j -th element potential:

$$\left(\frac{\partial G}{\partial n_j^*}\right)_{TP\mathbf{n}^*[j]} = \zeta_j, \quad (2.27)$$

where $\mathbf{n}^*[j]$ indicates all components of \mathbf{n}^* except the j -th one.

This potential is the Lagrange multiplier of the element according to the composition variables transformation (2.22), i.e. the conjugate of the resulting composition variable.

The potential *per particle* is

$$\frac{\zeta_j}{\mathcal{A}} = \left(\frac{\partial G}{\partial N_j^*}\right)_{TP\mathbf{N}^*[j]}, \quad (2.28)$$

where \mathcal{A} is the Avogadro's number. This value is the same for each particle of element j .

COMMENTS

α and, generically, φ are the states (of aggregation) of the j -th element particles. The various states can correspond to physical or chemical aggregation. Therefore, transitions are represented using the same symbols in both members. The species that do not change during transitions are called *elements*. Examples presented in the table specify what must be understood when speaking of elements and states (Luetich 2002a).

Table

Elements and states in five systems: (i) heterogeneous, (ii)-(iv) homogeneous

	system	states of A	states of B	states of C
(i)	$A_{(\text{liq})} \rightleftharpoons A_{(\text{vap})}$	liquid vapour	◦	◦
(ii)	$2 A \rightleftharpoons A_2$	free A_2	◦	◦
(iii)	$A + B \rightleftharpoons AB$	free AB	free AB	◦
(iv)	$\begin{cases} A + B \rightleftharpoons AB \\ 2 AB \rightleftharpoons B + A_2 B \end{cases}$	free AB $A_2 B$	free AB $A_2 B$	◦
(v)	$AC + B \rightleftharpoons C + AB$	AB AC	free AB	free AC

THIRD THEOREM**DYNAMIC EQUILIBRIUM AND THE ELEMENT POTENTIALS DEFINITION**

For systems showing no changes at the macroscopic level, the possible changes in aggregation states at the microscopic level are those which cause equal and opposite variations in their respective Gibbs functions.

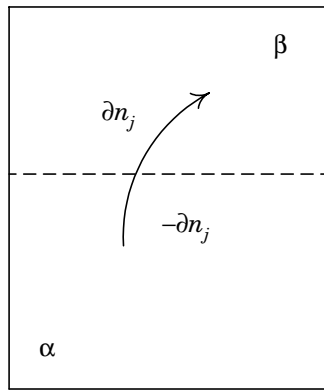
HYPOTHESIS

Let a system be at thermal, mechanic, and chemical equilibrium.

DEMONSTRATION

Let us suppose that a non-observable quantity of the j -th element atoms (particle) changes from the aggregation state α to the aggregation state β (figure 4). This transition would be associated to the following change in the Gibbs energy:

$$(dG)_{TP_{\mathbf{n}}^*} = \left(\frac{\partial G^\alpha}{\partial n_j^\alpha} \right)_{TP_{\mathbf{n}}^*} dn^\alpha + \left(\frac{\partial G^\beta}{\partial n_j^\beta} \right)_{TP_{\mathbf{n}}^*} dn^\beta. \quad (2.29)$$

**Figure 4**

Dynamics at microscopic level. Opposite variations of the j -th element mass in two states (α and β) in equilibrium

Since the Gibbs energy of the system can be written as follows:

$$G = G^\alpha + G^\beta + \sum_{\varphi} G^\varphi, \quad (2.30)$$

and, since the remaining states φ are not involved,

$$dG = dG^\alpha + dG^\beta. \quad (2.31)$$

Remembering the result of the Second Theorem and the property of derivatives

$$\left(\frac{\partial G}{\partial n} \right) = \left(\frac{-\partial G}{-\partial n} \right) = - \left(\frac{\partial G}{-\partial n} \right), \quad (2.32)$$

we obtain

$$\left(\frac{\partial G^\alpha}{\partial n_j^\alpha} \right)_{TP\mathbf{n}^*} = \left(\frac{\partial G^\beta}{\partial n_j^\beta} \right)_{TP\mathbf{n}^*}. \quad (2.33)$$

Given the relation between the potential and the fugacity concepts, this equation is the mathematic expression of the definition of fugacity as the "atoms" capacity to escape from an aggregation state.

Therefore, if

$$\partial n_j^\beta = -\partial n_j^\alpha, \quad (2.34)$$

the relation

$$\partial G^\alpha = -\partial G^\beta \quad (2.35)$$

can be obtained, which constitutes the *thermodynamic formalization* of the dynamic equilibrium idea.

This property is a consequence of the equality of the Lagrange multipliers for particles of the same element in two different states.

$$\zeta_j^\alpha = \mathcal{A} \left(\frac{\partial G}{\partial N_j^\alpha} \right)_{TPN^*} = \zeta_j^\beta = \mathcal{A} \left(\frac{\partial G}{\partial N_j^\beta} \right)_{TPN^*} \quad (2.36)$$

The effect of the movement of an unobservable particle on the Gibbs energy of the whole system is null.

$$(dG)_{TPN^*} = 0 \quad (2.37)$$

COMMENTS

In the First Theorem, it has been demonstrated that the equivalence of linearity and homogeneity gives rise to equality of potentials (zeroth order homogeneous properties).

The zeroth order homogeneity of the element potential μ :

$$\mu(\mathbf{x}, kn) = \mu(\mathbf{x}, n), \quad (2.38)$$

where \mathbf{x} is the vector of molar fractions $\mathbf{n}/\sum_i n_i$, is due to the fact that the element potential is the derivative with respect to a variable of a first order homogeneous function with respect to the same variable.

$$G(\mathbf{x}, kn) = k G(\mathbf{x}, n) \quad (2.39)$$

$$\frac{\partial G(\mathbf{x}, kn)}{\partial kn} = \frac{\partial [k G(\mathbf{x}, n)]}{k \partial n} = \frac{k \partial G(\mathbf{x}, n)}{k \partial n} = \frac{\partial G(\mathbf{x}, n)}{\partial n} \quad (2.40)$$

In an homogeneous system, both variables are homogeneous, but to the word *homogeneous* must be assigned a different sense: G is not changed by the number of particles being considered (otherwise, it is not changed by units: a mole is assigned so many calories as kilocalories correspond to a kilomole); μ , instead, has the same value in every point.

At this point, it is important to stress that partial molar properties have the same value as molar properties, not only in the case of pure bodies, but also when the system size is so large that the removal or addition of a small quantity of a component does not alter the composition.

At the atomic-molecular level, Leibnitz notation (and the whole infinitesimal calculus) is especially revealing.

In brief, in a system at equilibrium, the movement of particles from one aggregation state to another does not disagree with the thermodynamic laws of macroscopic systems.

The idea of dynamic equilibrium is closely related to the concept of *microscopic reversibility* (Luetich 2002c).

3. CONCLUSIONS

The condition of homogeneity of G with respect to \mathbf{n} is on the grounds of the whole reasoning that successively leads to: (1) the element potential definition; (2) the physical approach to equilibrium problems; and (3) the formalization of the equilibrium dynamics at the microscopic level. This is so because: (1) homogeneity is related to the linear feature of the Lagrange multipliers method; (2) Lagrange multipliers are the conjugate of the element composition variables; and (3) changes in the state of aggregation at the microscopic level do not modify the Gibbs energy of the system because, at equilibrium, element potentials are zeroth degree homogeneous properties.

The homogeneity condition is not so restrictive as we may think when considering the fact that we call a system *homogeneous* if its properties are *all* homogeneous, i.e. a phase. If we take any simple system in equilibrium and consider a number of particles n_i of each class, the Gibbs energy of that subsystem is G ; if we consider a quantity λn_i , the corresponding Gibbs energy is λG , independently of the aggregation state of the particles (figure 1). Therefore, the same reason that leads to defining element potentials, that is to say, homogeneity of G with respect to \mathbf{n} , also gives validity to the physical approach to equilibrium problems.

In multi-element systems, the potential of each of them is the derivative of the Gibbs energy with respect to the corresponding composition variable, keeping the remaining variables constant. In terms of variations (Leibnitz notation), an element potential is the quotient of the Gibbs energy change in relation to the change in the element composition variable: the idea of variation, i.e. of dynamics –even in closed systems– is implicit in the definition of potential. For that purpose, the remaining variables must be kept constant and mixing effects

avoided. But precisely, differential variations are the ones that avoid these effects, since they do not modify the overall composition. Not only is dynamics at microscopic level not forbidden by Chemical Thermodynamics formalization, but it is implicit in it.

ACKNOWLEDGEMENTS

This work was financially supported by FOMEC (Fondo para el Mejoramiento de la Calidad Universitaria, Secretaría de Políticas Universitarias, Ministerio de Cultura y Educación de la Nación, República Argentina), Project No. 824, and the Luventicus Academy of Sciences.

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