

II. LINEAR COMBINATIONS, LAGRANGE MULTIPLIERS, AND LEGENDRE TRANSFORMS—A LOOK AT THREE METHODS TO WRITE THE GIBBS ENERGY OF REACTIVE MIXTURES

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ABSTRACT

A comparison of three methods to deduce a property of element potentials that allows to write the Gibbs energy expression for systems at chemical equilibrium is presented. These methods are: (1) the algebraic procedure widely used in reactive distillation modelling to obtain the *transformed composition variables*, (2) the classical non-stoichiometric formulation of chemical equilibrium problems, and (3) the complete Legendre transformation of the Gibbs energy with respect to element composition variables. These three techniques lead to the same result in most cases, i.e. when elements are chosen among the system components. Because of its consistency with the rest of the Thermodynamics formalization, the latter gives deeper insight into the transformed composition variables and the auxiliary function of the Lagrange multipliers method. The element composition variables are the conjugate variables of the element potentials. The auxiliary function of the Lagrange multipliers method is the complete Legendre transform of the Gibbs energy with respect to element composition variables, and its value is zero for equilibrium states.

***Key index phrases:* Gibbs energy; chemical equilibria; linear combinations;
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1. INTRODUCTION

In reactive mixtures, changes in composition variables are not independent. Thus, for reactive closed systems, the differential form of the fundamental equation takes a simpler form than the one for open non-reactive systems (Luetich 2002). It has been demonstrated that this simplification is due to the fact that such variables can be transformed in others which do not change when the equilibrium is displaced modifying the state variables.

An algebraic method to carry out this transformation was introduced by Barbosa & Doherty (1987) with the purpose of transferring to reactive distillation techniques of non-reactive distillation modelling.

Pérez Cisneros *et al.* (1997) treated the same systems by means of the classical non-stoichiometric formulation (Smith & Missen 1991), showing that this method makes it possible to use composition variables which do not advance even in the case of reactions such as esterification, i.e. when not all the elements exist free in the mixture.

At the same time, Alberty (1997) presented a method based on the use of Legendre transformations to treat systems containing a component with constant chemical potential. His approach was based on previous works related to the reduction of the number of composition variables in systems containing pseudoisomers (Alberty & Oppenheim 1990).

In this work, it is demonstrated that using complete Legendre transformations of the Gibbs energy with respect to the element composition variables allows for a deeper interpretation of the physical sense of the transformed composition variables (Luetich 1999) and the auxiliary function of the Lagrange multipliers method (Luetich 2001).

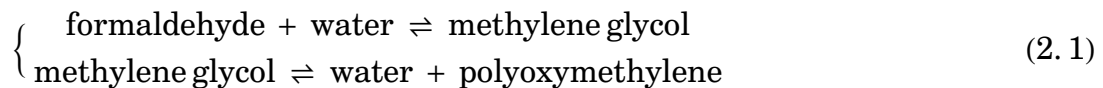
A comparison of the three techniques is done by applying them to the solution of a problem for which all lead to the same result.

This paper is the second of four related works written to clarify the concept of *microscopic reversibility*. With this purpose, the emphasis here is laid on the information contained in the different forms of the fundamental equation for reactive systems.

2. WRITING THE GIBBS ENERGY EXPRESSION

OUTLINE OF THE PROBLEM

Given the reactive system studied by Brandani & DiGiacomo (1984)



the simplest expression for the Gibbs energy is to be found.

SOLUTIONS

■ LINEAR COMBINATIONS

To simplify the notation, generic components A, B, C, and D, instead of formaldehyde, water, methylene glycol and polyoxymethylene, respectively, will be used.



The Gibbs energy of system (2.2),

$$G = (\mu_A \ \mu_B \ \mu_C \ \mu_D)(n_A \ n_B \ n_C \ n_D)^T, \quad (2.3)$$

at equilibrium, is subject to the restrictions

$$(\mu_A \ \mu_B \ \mu_C \ \mu_D) \begin{pmatrix} 1 & 0 \\ 1 & -1 \\ -1 & 2 \\ 0 & -1 \end{pmatrix} = (0 \ 0). \quad (2.4)$$

(This property accounts for the use of the adjective "chemical" for the magnitude μ .)

Then, only two chemical potentials are independent.

$$(\mu_A \ \mu_B) \begin{pmatrix} 1 & 0 \\ 1 & -1 \end{pmatrix} + (\mu_C \ \mu_D) \begin{pmatrix} -1 & 2 \\ 0 & -1 \end{pmatrix} = (0 \ 0) \quad (2.5)$$

$$(\mu_C \ \mu_D) = -(\mu_A \ \mu_B) \begin{pmatrix} 1 & 0 \\ 1 & -1 \end{pmatrix} \begin{pmatrix} -1 & 2 \\ 0 & -1 \end{pmatrix}^{-1} \quad (2.6)$$

C and D are the so-called *reference components* (Barbosa & Doherty 1987).

On the other hand, associating terms in the matricial expression of the Gibbs energy,

$$G = (\mu_A \ \mu_B)(n_A \ n_B)^T + (\mu_C \ \mu_D)(n_C \ n_D)^T. \quad (2.7)$$

The following step is the most important one since, by means of it, two variables are eliminated:

$$G = (\mu_A \ \mu_B) \begin{pmatrix} n_A + n_C + 2n_D \\ n_B + n_C + n_D \end{pmatrix}. \quad (2.8)$$

This relation allows to define the *transformed composition variables* (\hat{n}).

$$(\mu_A \ \mu_B) \begin{pmatrix} \hat{n}_A \\ \hat{n}_B \end{pmatrix} \triangleq G \quad (2.9)$$

In appendix A, it is shown that this procedure is equivalent to eliminate the degrees of advance of both reactions.

■ LAGRANGE MULTIPLIERS

The system can be viewed as constituted by "element" A and "element" B (physical approach):



Therefore, it is intended to minimize the function

$$G = G(T, P, (n_A \ n_B \ n_C \ n_D)), \quad (2.11)$$

subject to restrictions

$$\begin{pmatrix} n_A^* \\ n_B^* \end{pmatrix} = \begin{pmatrix} 1 & 0 & 1 & 2 \\ 0 & 1 & 1 & 1 \end{pmatrix} \begin{pmatrix} n_A \\ n_B \\ n_C \\ n_D \end{pmatrix}, \quad (2.12)$$

which define the composition variables n_A^* and n_B^* . These variables arise by inspecting the number of "atoms" that conforms each molecule.

The problem is just the classical minimisation one, with bound variables, solved by Lagrange using *multipliers*.

Let

$$\Phi = G - \left[(\lambda_A \quad \lambda_B) \begin{pmatrix} 1 & 0 & 1 & 2 \\ 0 & 1 & 1 & 1 \end{pmatrix} \right] \begin{pmatrix} n_A \\ n_B \\ n_C \\ n_D \end{pmatrix} \quad (2.13)$$

be the corresponding auxiliary function [the Lagrangian, $\Phi(\mathbf{n}, \lambda)$].

Its derivatives with respect to mole numbers are

$$\begin{pmatrix} \frac{\partial \Phi}{\partial n_A} \\ \frac{\partial \Phi}{\partial n_B} \\ \frac{\partial \Phi}{\partial n_C} \\ \frac{\partial \Phi}{\partial n_D} \end{pmatrix} = \begin{pmatrix} \mu_A \\ \mu_B \\ \mu_C \\ \mu_D \end{pmatrix} - \left[(\lambda_A \quad \lambda_B) \begin{pmatrix} 1 & 0 & 1 & 2 \\ 0 & 1 & 1 & 1 \end{pmatrix} \right]^T. \quad (2.14)$$

The matrix product should be transposed because

$$\begin{bmatrix} \frac{\partial}{\partial n_A} \\ \frac{\partial}{\partial n_B} \\ \frac{\partial}{\partial n_C} \\ \frac{\partial}{\partial n_D} \end{bmatrix} \begin{pmatrix} n_A \\ n_B \\ n_C \\ n_D \end{pmatrix} = \begin{bmatrix} (1 \ 0 \ 0 \ 0)^T \\ (0 \ 1 \ 0 \ 0)^T \\ (0 \ 0 \ 1 \ 0)^T \\ (0 \ 0 \ 0 \ 1)^T \end{bmatrix}. \quad (2.15)$$

These derivatives become null –giving G its minimum value– when

$$\begin{pmatrix} \mu_A \\ \mu_B \\ \mu_C \\ \mu_D \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \\ 1 & 1 \\ 2 & 1 \end{pmatrix} \begin{pmatrix} \lambda_A \\ \lambda_B \end{pmatrix} = \begin{pmatrix} \lambda_A \\ \lambda_B \\ \lambda_A + \lambda_B \\ 2\lambda_A + \lambda_B \end{pmatrix}. \quad (2.16)$$

Therefore,

$$\min G = (n_A + n_C + 2n_D \quad n_B + n_C + n_D) \begin{pmatrix} \lambda_A \\ \lambda_B \end{pmatrix}; \quad (2.17)$$

$$(n_A^* \quad n_B^*) \begin{pmatrix} \lambda_A \\ \lambda_B \end{pmatrix} \triangleq \min G. \quad (2.18)$$

The relation between both preceding methods is shown in appendix B.

■ LEGENDRE TRANSFORMS

For this reactive system, the Gibbs energy expression is

$$G = (n_A \ n_B \ n_C \ n_D) \begin{pmatrix} \mu_A \\ \mu_B \\ \mu_C \\ \mu_D \end{pmatrix}. \quad (2.19)$$

At constant T and P , the equation which determines the change of this magnitude with composition variables is

$$(dG)_{TP} = (\mu_A \ \mu_B \ \mu_C \ \mu_D) d \begin{pmatrix} n_A \\ n_B \\ n_C \\ n_D \end{pmatrix}. \quad (2.20)$$

Then, the problem consists of finding out the minimum number of times in which the Gibbs energy should be transformed when variables are bound by chemical reactions stoichiometry so as to obtain its complete Legendre transform. But this number is just the number of elements. In other words, variables that remain constant during a reaction are the element composition variables. Thus, the transformation (2.12) should be used.

For this case, the complete Legendre transform of G is

$$G - (n_A^* \ n_B^*) \begin{pmatrix} \zeta_A \\ \zeta_B \end{pmatrix} \triangleq G_{AB}^*. \quad (2.21)$$

[A new symbol (ζ) is introduced here because it is not known yet which variables should go with the transformed composition variables. Variables ζ are the *element potentials*.]

Operating on equations (2.21) and (2.12)

$$d \left(G - (n_A^* \ n_B^*) \begin{pmatrix} \zeta_A \\ \zeta_B \end{pmatrix} \right) = 0; \quad (2.22)$$

$$(\mu_A - \zeta_A \ \mu_B - \zeta_B \ \mu_C - \zeta_A - \zeta_B \ \mu_D - 2\zeta_A - \zeta_B) d \begin{pmatrix} n_A \\ n_B \\ n_C \\ n_D \end{pmatrix} = 0. \quad (2.23)$$

Since this equation holds for non null variations, we obtain the expressions for element and compound potentials:

$$(\mu_A \ \mu_B \ \mu_C \ \mu_D) = (\zeta_A \ \zeta_B \ \zeta_A + \zeta_B \ 2\zeta_A + \zeta_B). \quad (2.24)$$

Therefore,

$$G = (n_A^* \ n_B^*) \begin{pmatrix} \mu_A \\ \mu_B \end{pmatrix}. \quad (2.25)$$

This is the same result obtained by means of the Lagrange multipliers method. Note that this technique –using integral equations– is the inverse of the linear combinations method (appendix C).

From here on, to complete the deduction, it will be convenient to use the following notation:

$$(\mu_A - \zeta_A \ \mu_B - \zeta_B \ \mu_C - \zeta_A - \zeta_B \ \mu_D - 2\zeta_A - \zeta_B) \stackrel{\Delta}{=} (\mu_A^* \ \mu_B^* \ \mu_C^* \ \mu_D^*), \quad (2.26)$$

where μ^* is the transformed potential.

In addition, transformation (2.21) defines a thermodynamic potential whose expression in terms of the original and the transformed composition variables, is

$$G_{AB}^* = (0 \ 0 \ \mu_C - \mu_A - \mu_B \ \mu_D - 2\mu_A - \mu_B) \begin{pmatrix} n_A \\ n_B \\ n_C \\ n_D \end{pmatrix}; \quad (2.27)$$

$$G_{AB}^* = (0 \ 0 \ \mu_C^* \ \mu_D^*) \begin{pmatrix} n_A \\ n_B \\ n_C \\ n_D \end{pmatrix}, \quad (2.28)$$

which is zero at the equilibrium state.

Thus, the differential form of this function is

$$(dG_{AB}^*)_{TP} = -(n_A^* \ n_B^*) \begin{pmatrix} d\mu_A \\ d\mu_B \end{pmatrix}. \quad (2.29)$$

Formulae, which relate the transformed and the original thermodynamic potentials and their derivatives with the transformed composition variables for equilibrium states, are shown in table 1.

Table 1

Equilibrium conditions for the system $\begin{cases} A + B \rightleftharpoons C \\ 2C \rightleftharpoons B + D \end{cases}$, in terms of the Gibbs and the transformed Gibbs functions

$G = \min G = n_A^* \mu_A + n_B^* \mu_B \neq 0$	$G_{AB}^* = \min G_{AB}^* = \mu_C^* n_C + \mu_D^* n_D = 0$
$(dG)_{TP} = \mu_A dn_A^* + \mu_B dn_B^* = 0$	$(dG_{AB}^*)_{TP} = -n_A^* d\mu_A - n_B^* d\mu_B = 0$

Both functions (G and G_{AB}^*) have null differentials at equilibrium states, but only the transformed potential is zero. In the first case, the differential nullity is due to the invariability throughout the reaction of the transformed composition variables. In the second case, it is so, because the transformed composition variables are bound to potentials by a relationship analogous to the so-called *Gibbs-Duhem equation*.

■ Generalization

The general expression of the Gibbs energy for systems undergoing chemical reactions is

$$G = G(\mathbf{m}, \mathbf{n}) = \mathbf{n}^T \boldsymbol{\mu}, \quad (2.30)$$

where \mathbf{m} is the vector of the state variables and \mathbf{n} is the vector of the composition variables.

$$\mathbf{m} = (T, P) \quad (2.31)$$

Stoichiometric constraints reduce the number of composition variables:

$$\mathbf{C} \mathbf{n} = \mathbf{n}^*. \quad (2.32)$$

\mathbf{C} is the conservation matrix.

The intensive variables which go with the transformed composition variables in the shorten expression of the Gibbs energy can be related to chemical potentials.

$$G = (\mathbf{n}^*)^T \boldsymbol{\zeta} \quad (2.33)$$

$$\boldsymbol{\mu}^* = \boldsymbol{\mu} - \mathbf{C}^T \boldsymbol{\zeta} = 0 \quad (2.34)$$

The general integral and differential forms of the transformed Gibbs function are

$$G^* = (\boldsymbol{\mu}^*)^T \mathbf{n}; \quad (2.35)$$

$$(dG^*)_{\mathbf{m}} = -(\mathbf{n}^*)^T d\boldsymbol{\zeta}. \quad (2.36)$$

From equations (2.34), the components of $\boldsymbol{\zeta}$ can be obtained. When replacing them in equation (2.36), they provide the expression of dG^* according to the original chemical potentials (μ). The transformed potential results from equations (2.34). If they are replaced in equation (2.35), the integral expression of G^* can be obtained.

Otherwise, adding to equation (2.23) the Gibbs-Duhem equation,

$$(\boldsymbol{\mu}^*)^T d\mathbf{n} + \mathbf{n} d\boldsymbol{\mu} = 0; \quad (2.37)$$

$$[d(G - (\mathbf{n}^*)^T \boldsymbol{\zeta})]_{\mathbf{m}} = (dG^*)_{\mathbf{m}} = -(\mathbf{n}^*)^T d\boldsymbol{\zeta}. \quad (2.38)$$

Therefore, we obtain the equation:

$$(dG)_{\mathbf{m}} = \boldsymbol{\zeta}^T d\mathbf{n}^*, \quad (2.39)$$

whose importance is apparent when studying chemical equilibrium problems within the frame of the physical approach (Luetich 2002).

The transformed composition variables are the conjugate variables of the element potentials (Luetich 2001).

Table 2 presents a summary of the three methods used to solve this problem.

Table 2

One problem, three focuses

THE PROBLEM	ALTERNATIVE FORMS
Given the reactive system	<u>Linear combinations</u>
$\begin{cases} A + B \rightleftharpoons C \\ 2 C \rightleftharpoons B + D \end{cases}$	Transform the mole numbers of C and D
the simplest	to put them as combinations of
expression for the Gibbs	the ones of A and B in the expression of G .
energy is to be found.	$G = n_A \mu_A + n_B \mu_B + n_C \mu_C + n_D \mu_D$ $\begin{cases} \mu_A + \mu_B - \mu_C = 0 \\ -\mu_B + 2 \mu_C - \mu_D = 0 \end{cases}$
	<u>Lagrange multipliers</u>
	Using the element
	composition variables n_A^* and n_B^* ,
	give an expression to the minimum
	of the function
	$G = G(T, P, (n_A \ n_B \ n_C \ n_D)).$
	<u>Legendre transforms</u>
	Find the conjugates of element composition
	variables to write the differential form of
	$G = G(T, P, (n_A^* \ n_B^*)).$

3. CONCLUSIONS

In the method introduced by Barbosa and Doherty (1987), the composition variables come *after* defining the way in which chemical potentials will be combined (equilibrium condition). On the contrary, in the Lagrange multipliers and the Legendre transforms methods, the selection of variables to be used in describing the system composition is made *before* obtaining the expressions for potentials. That is what allows us to find a simple expression for the thermodynamic function that defines the equilibrium states in the case of reactions such as esterification (Pérez Cisneros *et al.* 1997), i.e when elements are always combined.

When "elements" are chosen in such a way that information on the system composition is not encoded –i.e. when elements and the reference species of the linear combinations method coincide– results converge and correspond to the same Legendre transformation.

The advantage of resorting to Legendre transformations lies on the fact that, during the demonstration, the physical sense of the variables remains explicit. This allows for an interpretation of the Lagrange auxiliary function, which has a clear physical meaning: it is the complete Legendre transform of the Gibbs energy with respect to the element composition variables, and its value is zero for equilibrium states.

The transformed composition variables are those linear combinations of such variables independent of the degrees of advance. They are also the conjugate variables of element potentials. These potentials are: (1) the intensive variables which go with certain mole number combinations (appendix A); (2) the Lagrange multipliers when minimizing the Gibbs energy subject to stoichiometric constraints; and (3) the conjugate of element composition variables when obtaining the complete Legendre transform of G .

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APPENDIX A

TRANSFORMED COMPOSITION VARIABLES AND DEGREES OF ADVANCE

Taking as a basis the system approached in section 2, here it will be demonstrated that the transformed composition variables are the linear combinations of the composition variables that turn out to be degree of advance-independent.

By separating from the initial quantities of B and C the ones participating in each reaction, we obtain

$$\xi_1 = \frac{n_C^1 - n_C^{01}}{-1} = \frac{n_A - n_A^0}{1} = \frac{n_B^1 - n_B^{01}}{1};$$

$$n_C^1 = n_C^{01} - \xi_1;$$

$$n_A = n_A^0 + \xi_1;$$

$$n_B^1 = n_B^{01} + \xi_1;$$

$$\xi_2 = \frac{n_B^2 - n_B^{02}}{-1} = \frac{n_D - n_D^0}{-1} = \frac{n_C^2 - n_C^{02}}{2};$$

$$n_B^2 = n_B^{02} - \xi_2;$$

$$n_D = n_D^0 - \xi_2;$$

$$n_C^2 = n_C^{02} + 2 \xi_2.$$

And, choosing adequate linear combinations of the composition variables,

$$\begin{aligned} n_A + n_C + 2 n_D &= n_A^0 + \xi_1 + n_C^{01} - \xi_1 + n_C^{02} + 2 \xi_2 + 2 (n_D^0 - \xi_2); \\ &= n_A^0 + n_C^0 + 2 n_D^0; \end{aligned}$$

$$\begin{aligned} n_B + n_C + n_D &= n_B^{01} + \xi_1 + n_B^{02} - \xi_2 + n_C^{01} - \xi_1 + n_C^{02} + 2 \xi_2 + n_D^0 - \xi_2; \\ &= n_B^0 + n_C^0 + n_D^0. \end{aligned}$$

No ξ corresponds to these variables: they do not advance.

Note that the key of this reasoning is the separation of the initial quantities of B and C into two parts whose extensions are *not* arbitrary.

APPENDIX B

COMPARISON OF TWO TRANSFORMATIONS

Transformations of composition variables in the Lagrange multipliers and the Legendre transforms techniques is *previous* to the application of these methods and can be written as follows:

$$\mathbf{C} \begin{pmatrix} n_A \\ n_B \\ n_C \\ n_D \end{pmatrix} = \begin{pmatrix} n_A^* \\ n_B^* \end{pmatrix}.$$

On the contrary, the transformation of the linear combinations technique is the *result* of the application of this technique and can be expressed as follows:

$$\begin{pmatrix} n_A \\ n_B \end{pmatrix} - \mathbf{B} \begin{pmatrix} n_C \\ n_D \end{pmatrix} = \begin{pmatrix} \hat{n}_A \\ \hat{n}_B \end{pmatrix}.$$

The circumstances in which they lead to the same result can be found solving the equation

$$\mathbf{C} \begin{pmatrix} n_A \\ n_B \\ n_C \\ n_D \end{pmatrix} = \begin{pmatrix} n_A \\ n_B \end{pmatrix} - \begin{pmatrix} b_{11} & b_{12} \\ b_{21} & b_{22} \end{pmatrix} \begin{pmatrix} n_C \\ n_D \end{pmatrix}.$$

The components of \mathbf{C} are

$$\begin{pmatrix} c_{11} & c_{12} & c_{13} & c_{14} \\ c_{21} & c_{22} & c_{23} & c_{24} \end{pmatrix} = \begin{pmatrix} 1 & 0 & -b_{11} & -b_{12} \\ 0 & 1 & -b_{21} & -b_{22} \end{pmatrix}.$$

Thus, they lead to the same result when matrix \mathbf{C} can be divided into a diagonal matrix and another one that is the opposite of \mathbf{B} , i.e. when elements are selected among the set of components.

APPENDIX C

DIFFERENTIAL AND INTEGRAL EXPRESSIONS IN THE LEGENDRE TRANSFORMATIONS TECHNIQUE

In section 2, the problem was solved by means of the Legendre transformations method, using differential equations. The same problem can be solved using these equations in their integral form. In this case, the method becomes the inverse of that introduced by Barbosa and Doherty (1987): given equations to obtain \mathbf{n}^* from \mathbf{n} , the goal is to obtain the relation between ζ and μ .

$$G - \left[(\zeta_A \quad \zeta_B) \begin{pmatrix} 1 & 0 & 1 & 2 \\ 0 & 1 & 1 & 1 \end{pmatrix} \right] \begin{pmatrix} n_A \\ n_B \\ n_C \\ n_D \end{pmatrix} = 0$$

$$(\mu_A - \zeta_A \quad \mu_B - \zeta_B \quad \mu_C - \zeta_A - \zeta_B \quad \mu_D - 2\zeta_A - \zeta_B) \begin{pmatrix} n_A \\ n_B \\ n_C \\ n_D \end{pmatrix} = 0$$

This condition must be fulfilled when not all mole numbers are null (trivial solution),

$$(\mu_A \quad \mu_B \quad \mu_C \quad \mu_D) = (\zeta_A \quad \zeta_B \quad \zeta_A + \zeta_B \quad 2\zeta_A + \zeta_B).$$

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