

I. THE GIBBS ENERGY FORM OF THE FUNDAMENTAL EQUATION FOR MULTI-PHASE MULTI-REACTION SYSTEMS WITHIN THE PHYSICAL APPROACH

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ABSTRACT

A general Gibbs energy representation of the fundamental equation for multi-phase multi-reaction systems is presented. The integral expression of the Gibbs energy comprises of as many terms as variables which have been chosen to describe the composition. The simplest set of composition variables is the one used in the physical approach to equilibrium problems. Within this frame, the differential form of the Gibbs energy for closed systems consists of two terms, like that corresponding to systems with invariable composition. The central point of the argument is the following property: at given conditions, the stable equilibrium state of any system is the particular state for which the potential of "element" i

$$\mu_i = \left(\frac{\partial G}{\partial n_i} \right)_{TP_{\mathbf{n}[i]}}$$

is independent of the state of the "atoms" taken to carry out the variation ∂n_i that, keeping unchanged the remaining variables, produces the variation ∂G . To prove this, the interpretation of the employed composition variables is facilitated by using the complete Legendre transformation of G , homogeneous function of \mathbf{n} , instead of the traditional, mathematically equivalent method of Lagrange multipliers. No difference is made between physical and chemical aggregation, i.e. between phase and combination changes. A modification of the *phase rule* expression is also discussed.

Key index phrases: fundamental equation; Gibbs energy; chemical potential; Chemical Thermodynamics; phase rule; Legendre transformations

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1. INTRODUCTION

The stoichiometry of chemical reactions imposes restrictions on the evolution of composition variables, that are not present when only physical transitions occur. Therefore, systems undergoing chemical reactions can be identified by means of a composition vector whose dimension is smaller than the one for the same systems when chemical reactions are inhibited.

Works related to the writing of fundamental equations for systems at chemical equilibrium were published by authors from different areas (Alberty & Oppenheim 1988, Norval *et al.* 1989, Ung & Doherty 1995). In this work, systems at simultaneous physical and chemical equilibrium are studied in order to highlight a property of the potentials of the elements that allows the Gibbs energy to take several forms, the simplest one being to the so-called *physical approach* to equilibrium problems.

These problems arise when modelling operations involving physical and chemical equilibria, like reactive distillation, reactions accelerated by using phase-transfer catalysts, and transitions in the solid state of interest for metallurgy.

This paper is the first member of a tetralogy conceived to give insight into the concept of *microscopic reversibility*. To this end, here emphasis will be placed on the role of the observer who describes the system composition.

2. THEORETICAL BACKGROUND

THE FUNDAMENTAL EQUATION

The combined First and Second Law of Thermodynamics for closed simple systems of invariable composition that traverse quasi-static paths performing only mechanical work is

$$dU = T dS - P dV. \quad (2.1)$$

When a natural law settles a relationship among variations of certain magnitudes, it is said that the function of the left-hand side has as its natural variables those of the right-hand side. Thus, for closed systems that only perform mechanical work, S and V are the natural variables of U .

An appropriate name for the internal energy would be: *constant function in the isentropic-isometric differential evolutions of closed systems.*

$$(dU)_{SV} = 0 \quad (2.2)$$

When the natural variables of a thermodynamic function are kept constant, the function remains also constant.

By transforming equation (2.1), we obtain another one that is important in other processes.

$$dU + d(PV) - d(TS) = dG = -S dT + V dP \quad (2.3)$$

G is the *constant function of the isothermic-isobaric quasi-static evolutions of closed simple systems.*

$$(dG)_{TP} = 0 \quad (2.4)$$

The integrated equations (2.1) and (2.3) are different forms of the *fundamental equation.*

$$U = U(S, V) \quad (2.5)$$

$$G = G(T, P) \quad (2.6)$$

For systems with invariable composition, if we know how the Gibbs function varies with temperature and pressure, we will have all the information needed to know whether a state is a stable equilibrium one or not.

Extending these conclusions to systems where composition changes is simple: it is done by adding the (mole) number of particles of those species constituting the system to the state variables.

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

The differential form of this representation of the fundamental equation is

$$dG = -S dT + V dP + \sum_{i=1}^C \left(\frac{\partial G}{\partial n_i} \right)_{TP\mathbf{n}[i]} dn_i, \quad (2.8)$$

where $\mathbf{n}[i]$ denotes the components of vector \mathbf{n} , except the i -th one, and C is the number of components.

However, in section 4 it will be shown that, by selecting the appropriate composition variables, equation (2.3) can be also used in this case.

LEGENDRE TRANSFORMATIONS

The name *Legendre transform* of the function

$$y = y(x) \tag{2.9}$$

is given to

$$q = q(p) \equiv y - p x, \tag{2.10}$$

where

$$p \equiv \frac{dy}{dx}. \tag{2.11}$$

Equations (2.9) and (2.10) contain the same information, i.e. they represent the same (convex) curve.

What is interesting about this transformation is that

$$dq = dy - x dp - p dx = -x dp. \tag{2.12}$$

Differentials of y and q have their variables exchanged.

x and p are called *conjugate variables*.

A Legendre transformation of a thermodynamic function is carried out with the purpose of obtaining another function with certain natural variables. This is especially useful when these variables have fixed values (Alberty 1997).

It should be noted that for closed systems, G is the complete Legendre transform of U .

In the textbook by Tester & Modell (1997), a detailed discussion on this technique is presented.

THE PHYSICAL AND THE CHEMICAL APPROACHES

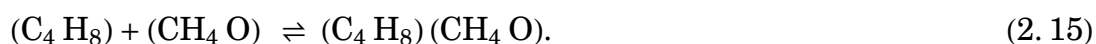
The mass balance of a closed reactive system can be expressed as follows (Smith & Missen 1991):

$$\mathbf{C} \boldsymbol{\nu} = \mathbf{0}, \quad (2.13)$$

where \mathbf{C} is the matrix that provides the number of atoms in each formula, $\boldsymbol{\nu}$ is the matrix of the stoichiometric coefficients, and $\mathbf{0}$ is the zero matrix.

In principle, these formulae are the ones that correspond to independent species (molecules, ions). But this is not the unique option. An "atom" can be the unit of any "element". Even "atoms" can be constituted by true atoms which are not physically together. This point was illustrated by Pérez Cisneros *et al.* (1997).

For example, the reaction of adding methanol to isobutene to form methyl *tert*-butyl ether (MTBE) studied by Smith *et al.* (1984), can be written in two ways:



The expression of the right-hand side of the second equation is not a structural formula, but it has the advantage of making it more evident that the reaction only involves two "elements".

The following \mathbf{C} and $\boldsymbol{\nu}$ matrices correspond to equation (2.14).

$$\mathbf{C}_1 = \begin{pmatrix} 4 & 1 & 5 \\ 8 & 4 & 12 \\ 0 & 1 & 1 \end{pmatrix} \quad (2.16)$$

$$\boldsymbol{\nu} = \begin{pmatrix} 1 \\ 1 \\ -1 \end{pmatrix} \quad (2.17)$$

It is easy to prove that they fulfill condition (2.13).

A simpler \mathbf{C} matrix corresponds to equation (2.15).

$$\mathbf{C}_2 = \begin{pmatrix} 1 & 0 & 1 \\ 0 & 1 & 1 \end{pmatrix} \quad (2.18)$$

In this case, condition (2.13) is also met.

In the first case (*chemical approach*), the composition vector consists of three components ($n_{\text{C}_4 \text{H}_8}$, $n_{\text{CH}_4 \text{O}}$, $n_{\text{C}_5 \text{H}_{12} \text{O}}$); in the second one (*physical approach*) it consists of two components ($n_{\text{C}_4 \text{H}_8}^*$, $n_{\text{CH}_4 \text{O}}^*$). Here the asterisk denotes reference

to the element. The number of "elements" (E) can be obtained by subtracting the stoichiometric restrictions (R) from the number of components (C).

$$E = C - R \quad (2.19)$$

[Not very frequent cases, in which mechanistic restrictions must be considered, have been pointed out by Smith (1979). In reactive distillation, there always exist a way to describe the composition of the system by means of magnitudes whose values don't change.]

According to the above discussion, variables can be classified as follows:

$$\left. \begin{array}{ll} \text{composition variables} & (\text{what-how much}) \\ \text{state variables} & (\text{how}) \end{array} \right\} \text{thermodynamic variables}$$

3. THE TRANSFORMATION OF THE COMPOSITION VARIABLES

In this section, the system (2.14), previously studied by Pérez Cisneros *et al.* (1997) using Lagrange multipliers, is treated by means of another equivalent technique –a variant of the one introduced by Alberty (1997)– (Luetich 2002b).



To simplify the notation, generic components A, B, and C, instead of isobutene, methanol, and methyl *tert*-butyl ether, respectively, will be used.

The transformation

$$\begin{pmatrix} n_A^* \\ n_B^* \end{pmatrix} \triangleq \begin{pmatrix} 1 & 0 & 1 \\ 0 & 1 & 1 \end{pmatrix} \begin{pmatrix} n_A \\ n_B \\ n_C \end{pmatrix} \quad (3.2)$$

defines the composition variables n_A^* and n_B^* . This relation can be obtained by inspection of the quantity of "atoms" that make up each molecule (matrix \mathbf{C}_2). Therefore, the values of these new variables do not change throughout the reaction; they coincide with the *transformed composition variables* (Barbosa & Doherty 1987).

For this system, the Gibbs energy expression is

$$G = n_A \mu_A + n_B \mu_B + n_C \mu_C . \quad (3.3)$$

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

$$(dG)_{TP} = \mu_A dn_A + \mu_B dn_B + \mu_C dn_C. \quad (3.4)$$

In addition, for example,

$$(dG_C)_{TP} \stackrel{\Delta}{=} [\partial(G - n_C \mu_C)]_{TP} \quad (3.5)$$

$$= d(n_A \mu_A + n_B \mu_B + n_C \mu_C) - \mu_C dn_C - n_C d\mu_C; \quad (3.6)$$

$$(dG_C)_{TP} = \mu_A dn_A + \mu_B dn_B - n_C d\mu_C. \quad (3.7)$$

This was a first-order Legendre transformation of the original function.

As equation (3.4) gives a relation between the variations of G and the variations of the composition variables, its complete Legendre transform will give a relation between the variations of potentials.

The complete Legendre transform of G with respect to the (constant) element composition variables is

$$G - n_A^* \zeta_A - n_B^* \zeta_B \stackrel{\Delta}{=} G_{AB}^*. \quad (3.8)$$

Here, ζ is the symbol used to represent the variables which go with the transformed composition variables.

G_{AB}^* is the constant null function in the quasi-static isothermic-isobaric evolutions of this system.

$$(dG_{AB}^*)_{TP} = 0 \quad (3.9)$$

Replacing definition (3.8),

$$d(n_A \mu_A + n_B \mu_B + n_C \mu_C - n_A^* \zeta_A - n_B^* \zeta_B) = 0; \quad (3.10)$$

$$(\mu_A - \zeta_A) dn_A + (\mu_B - \zeta_B) dn_B + (\mu_C - \zeta_A - \zeta_B) dn_C = 0. \quad (3.11)$$

Since this equation holds true when not all these variations are null:

$$\mu_A = \zeta_A; \quad (3.12)$$

$$\mu_B = \zeta_B; \quad (3.13)$$

$$\mu_C = \zeta_A + \zeta_B, \quad (3.14)$$

which proves that, at the stable equilibrium state, the potential of a free element is equal to the one of the combined element. This is what has been demonstrated in another way by Beattie & Oppenheim (1979).

Therefore,

$$G = n_A^* \mu_A + n_B^* \mu_B. \quad (3.15)$$

It should be noted that the transformation of "chemical" potentials μ_A and μ_B does not result in other chemical potentials. In fact, there is no property for the potentials of the elements equivalent to:

$$\mu_A + \mu_B - \mu_C = 0, \quad (3.16)$$

because, when working with elements, it does not make sense to talk about chemical reactions. Thus, an appropriate name for these magnitudes would be *element potentials*.

GENERALIZATION

The general expression of the Gibbs energy for reactive systems is

$$G = \mathbf{n}^T \boldsymbol{\mu}, \quad (3.17)$$

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

Stoichiometric constraints reduce the number of composition variables:

$$\mathbf{C} \mathbf{n} = \mathbf{n}^*. \quad (3.18)$$

Here, \mathbf{n}^* is the element composition vector.

The intensive variables ($\boldsymbol{\zeta}$) which go with the transformed composition variables in the shorten expression of the Gibbs energy,

$$G = (\mathbf{n}^*)^T \boldsymbol{\zeta}, \quad (3.19)$$

can be related to chemical potentials:

$$\boldsymbol{\mu} = \mathbf{C}^T \boldsymbol{\zeta} \quad (3.20)$$

If we take as "elements" a subset of the system components, $\boldsymbol{\zeta}$ will be a subset of $\boldsymbol{\mu}$.

4. A PROPERTY OF THE ELEMENT POTENTIALS

Here, the most important conclusion of the argument given in section 3 is used to introduce and comment on a general statement (Luetich 2002a).

At stable equilibrium states, the potential of an element is independent of the aggregation state (surroundings) of the particles being considered to carry out the variation ∂n_i which, keeping constant the remaining variables, produces the variation ∂G .

Let α and β be two certain aggregation states of the particles of species A in equilibrium by the transition t :



For any transition, the equilibrium condition is

$$\left(\frac{\partial G}{\partial \xi} \right)_{TP} = 0, \quad (4.2)$$

where ξ is the degree of advance of the transition.

The Gibbs free energy corresponding to a differential composition change is

$$\Delta_t G = \sum_k v_k \left(\frac{\partial G}{\partial n_k} \right)_{TP\mathbf{n}[k]} = 0. \quad (4.3)$$

Then,

$$\left(\frac{\partial G}{\partial n_A^\alpha} \right)_{TP\mathbf{n}_i^{[\alpha]}} = \left(\frac{\partial G}{\partial n_A^\beta} \right)_{TP\mathbf{n}_i^{[\beta]}}, \quad (4.4)$$

where φ is a generic aggregation state and i is a generic component.

Superscripts α and β could correspond to *any* aggregation state. That is to say, it doesn't matter which is the state (phase or chemical aggregate) where the variation in mole number is carried out, the change in the system Gibbs energy is the same.

COMMENTS

A single-component system with two phases in equilibrium (α and β) fulfill the condition:

$$\mu_A^\alpha = \mu_A^\beta = \mu_A. \quad (4.5)$$

However, there is no conceptual difference between physical and chemical aggregation. This can be made evident by the difficulty in setting down a limit between them. That is why there is a study field called *Chemical Thermodynamics*. Its historical origin must be traced to the attempts to transfer the results of phase transitions thermodynamics developed by Gibbs (1875-1878) –a physicist– to the energetic studies on chemical reactions carried out by van't Hoff and other physical chemists in the last decades of the nineteenth century (appendix A).

The importance of the above statement lies on the fact that because of the employed notation and nomenclature, the results are valid for any transition: if \mathbf{n}_A is the vector of the mole number of element A in each phase (primary interpretation), α , β , and generically φ will be the phases, and the equilibrium will be a physical equilibrium. But if \mathbf{n}_A is the vector of the mole number of element A in each compound (secondary interpretation), α , β , and φ will be the compounds and the equilibrium under analysis will be a chemical one.

With this notation, the composition of a multi-phase multi-component system is a vector of vectorial components, i.e. a matrix (\mathbf{n}), vector of components \mathbf{n}_i of components n_i^φ .

Let us assume that we have a vapour-liquid system constituted by A, B and C=AB.

The following equilibria are present



As shown in figure 1, if the emphasis is placed on the division made by the interphasial surface, a composition vector like the following one will be used for component A:

$$\mathbf{n}_A = (n_A^L, n_A^V) \quad (4.7)$$

where n_A^L and n_A^V are the number of particles of element A in the liquid and the vapour phases respectively.

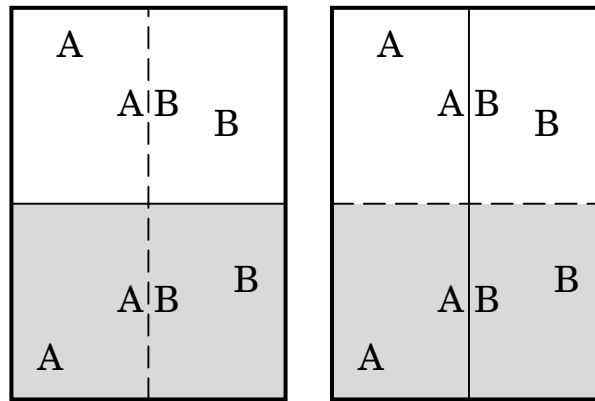


Figure 1

Two ways to define the composition of the system: $A+B \rightleftharpoons C$:
paying attention to phases or to elements

But if the focus is on element A, a different composition vector will be defined:

$$\mathbf{n}_A = (n_A^{\text{free}}, n_A^C) \quad (4.8)$$

where n_A^{free} is the number of free particles of element A and n_A^C is the number of particles of element A combined in C.

The conclusion is valid for both cases.

Nevertheless, in the first case,

$$\mathbf{n} = (\mathbf{n}_A, \mathbf{n}_B, \mathbf{n}_C); \quad (4.9)$$

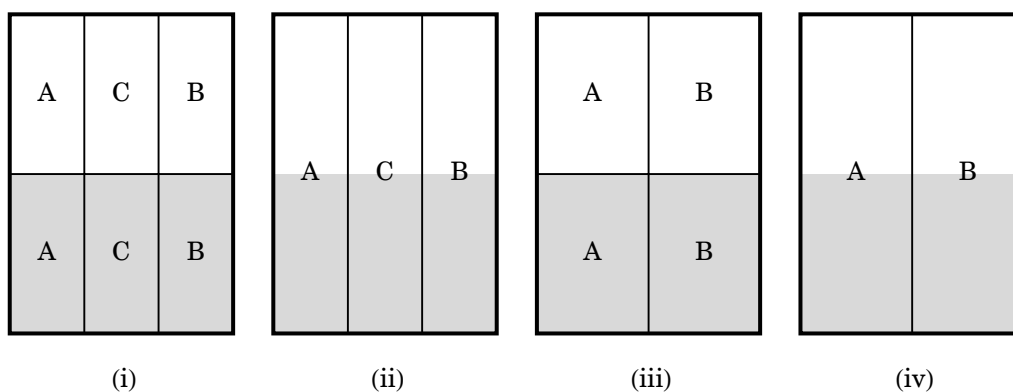
while in the second one,

$$\mathbf{n} = (\mathbf{n}_A, \mathbf{n}_B). \quad (4.10)$$

Therefore, by adopting the second criterion we deal with two less variables.

Phases, within the chemical approach, play the same role as components in the physical approach. Moreover, in the physical approach, there is no difference between phases and compounds: they are both aggregates of "atoms".

In summary, the composition can be described at four levels (figure 2), considering particles of different species: (i) those in different phases (Smith & Missen 1991) or combination states, (ii) those in different combination states, (iii) those in different phases, or (iv) those of different elements.

**Figure 2**

One system: $A+B \rightleftharpoons C$; four observers, who discriminate:

(i) phases and components, (ii) components, (iii) phases and elements, (iv) elements

The following expressions of the Gibbs energy correspond to each of the mentioned levels.

$$\begin{aligned}
 \text{(i)} \quad G &= n_A^L \mu_A^L + n_A^V \mu_A^V + n_B^L \mu_B^L + n_B^V \mu_B^V + n_C^L \mu_C^L + n_C^V \mu_C^V \\
 \text{(ii)} \quad G &= n_A \mu_A + n_B \mu_B + n_C \mu_C \\
 \text{(iii)} \quad G &= n_A^{*L} \mu_A^L + n_A^{*V} \mu_A^V + n_B^{*L} \mu_B^L + n_B^{*V} \mu_B^V \\
 \text{(iv)} \quad G &= n_A^* \mu_A + n_B^* \mu_B
 \end{aligned} \tag{4.11}$$

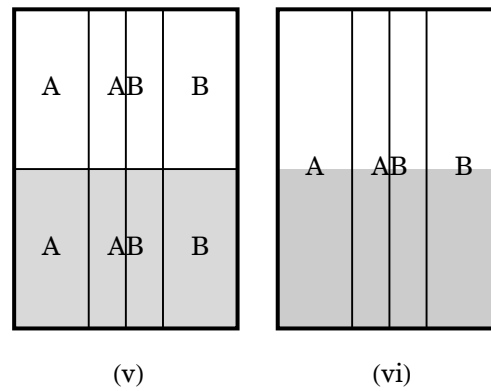
Expressions (ii), (iii) and (iv) were obtained from (i) through the relations showed in table 1.

Table 1

Formulae for converting the Gibbs energy expressions of the two-phase system $A+B \rightleftharpoons C$. φ = phase (L or V)

(i) → (ii)	$\mu_i^V = \mu_i^L$ $n_i^L + n_i^V = n_i$
(i) → (iii)	$\mu_A^\varphi + \mu_B^\varphi = \mu_C^\varphi$ $n_A^\varphi + n_C^\varphi = n_A^{*\varphi}$ $n_B^\varphi + n_C^\varphi = n_B^{*\varphi}$
(i) → (iv)	$\mu_i^V = \mu_i^L$ $\mu_A^\varphi + \mu_B^\varphi = \mu_C^\varphi$ $n_A^L + n_A^V + n_C^L + n_C^V = n_A^*$ $n_B^L + n_B^V + n_C^L + n_C^V = n_B^*$

If a still more detailed description had been made (figure 3), expressions of eight (v) and four (vi) terms would have been obtained. Schemes i-vi work as matrices.

**Figure 3**

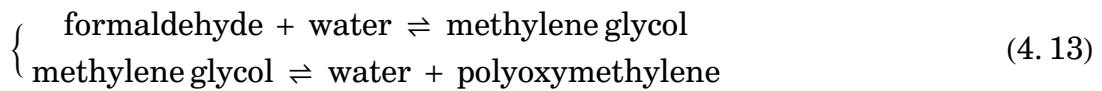
More detailed descriptions of the system $A+B \rightleftharpoons C$:

(v) phases, elements and states of combination, (vi) elements and states of combination

Not always, observer (ii) employs less terms to write the Gibbs energy expression than observer (iii). For this system,

$$\text{phases} \times \text{elements} > \text{components}, \quad (4.12)$$

but for the system studied by Brandani & DiGiacomo (1984)



which in the physical approach is



$$\text{phases} \times \text{elements} = \text{components} = 4. \quad (4.15)$$

A NOTE ON THE PHASE RULE

From the above discussion,

$$\text{species} = \text{terms in the Gibbs energy expression}. \quad (4.16)$$

Nevertheless, the number of variables, which when fixed, determine if the state of the system is a stable equilibrium one or not (state variables), is independent of the observer.

The number of free variables (F) is the number of species (σ) plus 2, less the number of phases (ϕ), and physical (R_{ph}) and chemical (R_{ch}) restrictions (transitions).

$$F = \sigma + 2 - \phi - R_{\text{ph}} - R_{\text{ch}} \quad (4.17)$$

Here R_{ph} is the number of restrictions of a physical nature. R_{ch} is the number of stoichiometric restrictions (R).

The values of these variables for observers i-vi is shown in table 2 ($\phi = 2$).

Table 2

Species (σ), physical restrictions (R_{ph}), and chemical restrictions (R_{ch}), for the system $A+B \rightleftharpoons C$.
Free variables (F) = 2

observer	i	ii	iii	iv	v	vi
σ	6	3	4	2	8	4
R_{ph}	3	0	2	0	6	2
R_{ch}	1	1	0	0	0	0

Figure 4 illustrates what it should be viewed as a physical constraint.

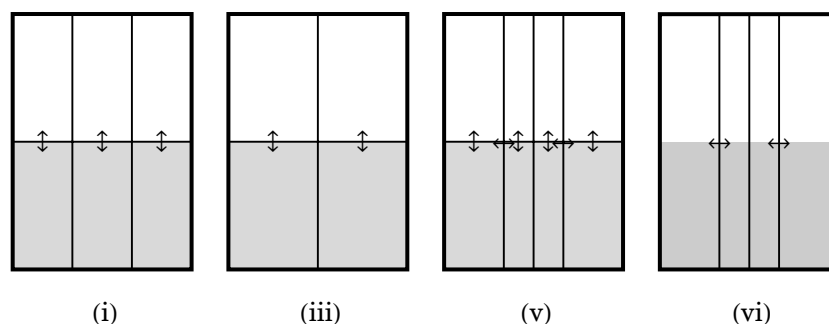


Figure 4

Physical and chemical restrictions of the system $A+B \rightleftharpoons C$:
Vertical and horizontal adjacency

R_{ph} is the term which connects the two approaches.

Formula (4.17) can also be deduced in a slightly different way than that used by J. Willard Gibbs (appendix B) and is analogous to the one given by Denbigh (1966) for a single observer:

$$F = C + 2 - \phi - R. \quad (4.18)$$

Here, the stoichiometric constraints can be associated with physical constraints or with components.

$$F = C + 2 - (\phi + R) = E + 2 - \phi \quad (4.19)$$

Note that magnitude $F + \phi - 2$ is the same for any observer.

$$\sigma - R_{\text{ph}} - R_{\text{ch}} = E \quad (4.20)$$

THE FUNDAMENTAL EQUATION FOR CLOSED SYSTEMS

For the reactive system (3.1) the number of natural variables of the transformed Gibbs energy is 4.

$$G_{\text{AB}}^* = G_{\text{AB}}^*(T, P, \mu_{\text{A}}, \mu_{\text{B}}) \quad (4.21)$$

It is not necessary to include the potential of species C, because:

$$\mu_{\text{C}} = \mu_{\text{A}} + \mu_{\text{B}}. \quad (4.22)$$

The minimum number of natural variables for the Gibbs energy is also 4.

$$G(T, P, (n_{\text{A}}^*, n_{\text{B}}^*)) \quad (4.23)$$

With no loss of generality, this fact can be shown by placing together the definitions (3.2) and the equation of the equilibrium constant (K) for a mixture of ideal gases:

$$K = K_y P^{\Delta\nu} = \frac{n_{\text{C}}}{n_{\text{A}} n_{\text{B}}} (n_{\text{A}} + n_{\text{B}} + n_{\text{C}}) \frac{1}{P}. \quad (4.24)$$

In other words, the rank of \mathbf{C}^{T} –which relates $\boldsymbol{\mu}$ and $\boldsymbol{\zeta}$ – is equal to the rank of \mathbf{C} –which relates \mathbf{n} and \mathbf{n}^* –.

In general, the number of equations (3.2) is E and the number of equations like (4.24) is R . The total is $E+R = C$. Given the components of \mathbf{n}^* , the components of \mathbf{n} are univocally determined.

Thus, taking into account the property of element potentials deduced in section 3, the Gibbs energy form of the fundamental equation for multi-phase multi-reaction closed systems observed by someone who does not distinguish nothing but elements is

$$G = G(T, P, \mathbf{n}^*) = \sum_{i=1}^E \mu_i n_i^* = \sum_{i=1}^E \left(\frac{\partial G}{\partial n_i^*} \right)_{TP\mathbf{n}^*[i]} n_i^*. \quad (4.25)$$

And its differential form,

$$dG(T, P, \mathbf{n}^*) = -S dT + V dP, \quad (4.26)$$

is valid even when the system contains inert components or catalysts, because their variables remain unchanged throughout transformations like (3.18). [The extensive variables G , S , and V relate to the whole system.]

Equations (4.25) and (4.26) hold for any simple closed system, i.e. for systems which are devoid of any internal boundaries and not acted upon by external force fields or inertial forces (Tester & Modell 1997).

For example, if system (3.1) also contains the inert component 1-butene (Smith *et al.* 1984),

$$\mathbf{n}^* = \begin{pmatrix} n_A^* \\ n_B^* \\ n_D^* \end{pmatrix} = \begin{pmatrix} 1 & 0 & 1 & 0 \\ 0 & 1 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} n_A \\ n_B \\ n_C \\ n_D \end{pmatrix} \quad (4.27)$$

As the number of moles of species D (1-butene) remains unchanged during the reaction, the Gibbs energy should be also transformed according to definition (3.8), i.e. not transforming the D-element variables:

$$G = n_A \mu_A + n_B \mu_B + n_C \mu_C + n_D \mu_D \quad (4.28)$$

$$dG(T, P, (n_A^*, n_B^*, n_D)) = -S dT + V dP \quad (4.29)$$

In summary, for closed systems, T and P are the natural variables of G [equation (2.3)], i.e. G can be represented as a surface in the 3D-space.

THE VARIABLES OF ELEMENT POTENTIALS

The problem: Which are the variables of μ_i in equation (4.25)?, can be solved in two different ways:

- i. The same variables as its primitive G , i.e. T , P , and \mathbf{n}^* .
- ii. At given T and P , for each phase there is a relation between potentials and composition.

$$\begin{cases} \mu^L = \mu^L(\alpha \mathbf{n}^L) \\ \mu^V = \mu^V(\beta \mathbf{n}^V) \end{cases} \quad (4.30)$$

Here, α and β are positive real numbers.

The phase equilibrium condition is:

$$\boldsymbol{\mu}^L = \boldsymbol{\mu}^V = \boldsymbol{\mu}, \quad (4.31)$$

and there exists a relation between the compositions of both phases:

$$\alpha \mathbf{n}^L = \alpha \mathbf{n}^L (\beta \mathbf{n}^V). \quad (4.32)$$

Therefore, being

$$\alpha \mathbf{n}^L + \beta \mathbf{n}^V = \mathbf{n}, \quad (4.33)$$

given \mathbf{n} , \mathbf{n}^L and \mathbf{n}^V are determined: there is only one equilibrium state. (This is one of the basis of the application to phase equilibrium of the so-called *Monte Carlo method*.)

THE FUNDAMENTAL EQUATION FOR OPEN SYSTEMS

The differential form of the fundamental equation for open systems is

$$dG(T, P, \mathbf{n}^*) = -S dT + V dP + \sum_{i=1}^E \mu_i dn_i^*. \quad (4.34)$$

In this case, T , P , and n_i^* are also the variables of G and μ_i . (It doesn't matter how fast reactions are; quasi-static processes are slow enough to allow equilibrium to be reached.)

For multi-phase systems, the composition of the currents leaving [entering] does not depend only on the characteristics of the exit [entrance] but also on its position. In batch reactive distillation operations, for example, the mixture leaves the distiller in the vapour state. In other experiments, selective membranes allow certain components to leave or enter the system.

5. CONCLUSIONS

The species to be used to describe the composition of a reactive system were chosen *before* performing the Legendre transformation of the Gibbs function. There is an arbitrary aspect in this selection, and the final form of the thermodynamic equations is conditioned by this contribution of the system observer (figure 5). As a consequence, expressions like (4.26) should indicate not only the system but also the observer characteristics (\mathbf{n}^*). If a simple expression is to be found for that thermodynamic function defining stable equilibrium states, the best choice for the composition variables is the element one, since in every reactive system, the quantity of each element remains constant.

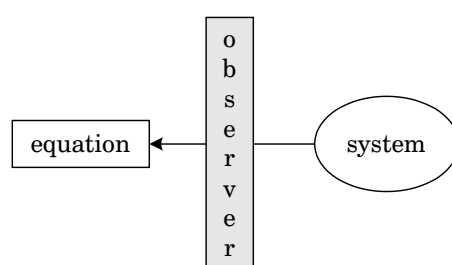


Figure 5

The role of the system observer

Following the discussed procedure, when dealing with reactive systems, the left-hand side of equation (2.1) must be modified, and not the right-hand side as was done to obtain equation (2.8). There always exists a way to identify a system by means of a set of constant composition variables.

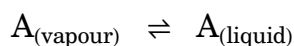
Sometimes, because of limitations in the analytic technique –case of certain isomers determined by chromatography– groups of components are quantified as a single one. In other cases, it is very difficult to discriminate phases –case of reactions beginning in a medium containing small drops which then become a microemulsion, and then a solution. This fact reduces the options when selecting composition variables. Nevertheless, in most cases, the final decision on which species are to be used to describe the composition is up to the observer.

If a reaction occurs while an inert substance is present, the corresponding term will not be transformed, since such a substance could be considered as a separate system.

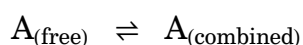
For any closed simple system, T and P are the natural variables of G and this thermodynamic function can be represented as a surface in the 3D-space. For open systems, G is a hypersurface in the $(3+E)D$ -space, and the differential form of the fundamental equation can be obtained adding the terms corresponding to element work [equation (4.34)].

The potential of an element does not depend at equilibrium on its particles state (environment), is a characteristic of the element. (This is also the answer to the question: Why can the "atoms" of an "element" be constituted by physically separate atoms?) If a system contains the same element in two different states, the corresponding potentials are equal. Taking this property into account helps us in modelling the element potential at the most convenient conditions, as we do when we calculate by means of ab initio methods the Gibbs energy of a pure gas at its saturation pressure instead of that of the liquid. Moreover, even when modelling, the former requires modelling the latter and vice versa –case of mixtures– this property can help us to carry out data-consistency tests.

By concept, there is no difference between physical and chemical aggregation. For any element A, transitions



and



are then comparable. Any transition is a *(pseudo)isomerisation*.

In the physical approach, the expression of the phase rule should be modified to obtain another one useful when no difference is made between physical and chemical aggregation [equation (4.17)]. An appropriate name for it would be *physico-chemical constraints rule*.

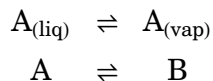
ACKNOWLEDGEMENTS

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APPENDIX A

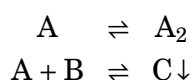
THE MIXING OF PRODUCTS

The difference between the following transitions:



is that in the phase transition, vapour and liquid are in different phases, while in the isomerisation A and B are mixed. The first transition is of a physical nature, and the second one –which we represent changing names– is a transition of a chemical nature.

The following are examples of opposite cases.

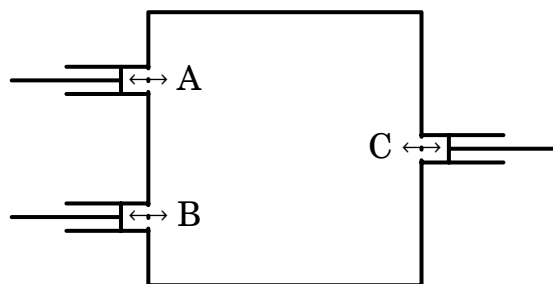


Here, monomer and dimer are mixed, and C is separate from the mixture of A and B.

A value for the Gibbs energy can be assigned to a mass of any component in any state (free, combined, mixed). If we want to separate components in transitions like



to study only chemical aggregation, we will need to make a *thought experiment* like that introduced by van't Hoff (figure 6). The so-called *van't Hoff chamber*, is a chamber held at a constant temperature and pressure which works as a reversible reactor where pure substances ingress and leave through selective membranes at their partial pressures.



The van't Hoff chamber, a reversible reactor.

A, B, and C enter and leave the reactor through selective membranes at their partial pressure

APPENDIX B**LEGENDRE TRANSFORMATIONS AND THE PHASE RULE**

The complete Legendre transform of function

$$G = G(T, P, \mathbf{n}),$$

with respect to the composition variables, is the function

$$G^* = G^*(T, P, \boldsymbol{\mu}),$$

which contains the same information about equilibrium, i.e. about intensive properties.

This is equivalent to say that

$$\underline{G} = \underline{G}(T, P, \boldsymbol{\mu}),$$

where \underline{G} is the molar Gibbs energy.

However –as was shown by J. Willard Gibbs– the latter one is preferable to deduce the *phase rule* (Denbigh 1966).

The traditional use of components leads to C (dimension of $\boldsymbol{\mu}$) plus 2 (T and P) variables in both cases. The Gibbs-Duhem equation, reduces in 1 the number $C+2$ for each phase, because phases differ in their composition but not in their element potentials (equations are linearly independent). Moreover, each independent reaction establishes a relation between chemical potentials and reduces in 1 the number of free variables [equation (4.18)] (Denbigh 1966).

When we consider particles in different states as particles of different species, each transition –physical or chemical– is a restriction and reduces in 1 the number $\sigma+2-\phi$ [equation (4.17)].

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