

# Novel Formulation of the Gibbs–Energy Change in Terms of Stoichiometrically Unique Response Reactions

Ilie Fishtik<sup>a</sup>, István Nagypál<sup>b</sup>, and Ivan Gutman<sup>b,c</sup>

<sup>a</sup> Institute of Chemistry, Academy of Sciences of Moldova, 277028 Kishinev, str. Academiei 3, Republica Moldova

<sup>b</sup> Institute of Physical Chemistry, Attila József University, H-6701 Szeged, P. O. Box 105, Hungary

<sup>c</sup> on leave from Faculty of Science, University of Kragujevac, Kragujevac, Yugoslavia

Z. Naturforsch. **51 a**, 1079–1083 (1996); received July 9, 1996

The equation for the change of Gibbs energy in complex chemical systems is reformulated in terms of the newly conceived response reactions (RERs). The present formulation has the remarkable property of being unique: the composition of the species unequivocally determines the response reactions and via them the change of the Gibbs energy of the system. Furthermore, it enables one to reinterpret and rationalize some basic concepts of chemical thermodynamics, as coupling between reactions, sensitivity coefficients, etc.

**Key words:** Chemical thermodynamics; Sensitivity analysis; Response reactions; Thermodynamic coupling (of chemical reactions)

## Introduction

There are two equivalent equations describing the chemical transformations in a closed system containing  $n$  species, in terms of the Gibbs energy:

$$dG_{(T,P)} = \sum_{i=1}^n \mu_i dn_i, \quad (1)$$

$$dG_{(T,P)} = - \sum_{j=1}^m A_j d\xi_j. \quad (2)$$

The first equation is the original Gibbs formulation [1], given in terms of chemical potentials ( $\mu_i$ ) and the amounts ( $n_i$ , number of moles) of the species  $i = 1, 2, \dots, n$ . The second one represents the De Donder approach [2] in terms of affinities ( $A_j$ ) and extents ( $\xi_j$ ) of the stoichiometrically independent reactions (SIRs)  $j = 1, 2, \dots, m$ .

Calculations based on (1) regard the system as a whole, the actual change of Gibbs energy is not decomposed into contributions associated with individual reactions. The second equation makes it possible

to express the actual change of  $G$  as a sum of contributions associated with particular SIRs. The concept of affinity is the basis of the De Donder theorem, describing the time development of chemical processes:

$$\sum_{i=1}^m A_i \frac{d\xi_i}{dt} = \sum_{i=1}^m A_i v_i \geq 0. \quad (3)$$

The condition of equilibrium in this formulation is

$$A_i = 0; \quad v_i = \frac{d\xi_i}{dt} = 0. \quad (4)$$

The problem with (2) is that the choice of the SIRs is arbitrary, there are no criteria for selecting a unique set of them. This, in turn, is the cause of the criticism [3,4] of the idea of thermodynamic coupling [5,6] between chemical reactions and of the ambiguous definition of reaction velocities in complex reacting systems [6].

We recently put forward the concept of *response reactions* (RERs) [7–9], which enabled the rationalization of some unusual behavior of equilibrium systems [7, 9], interpretation of cases in which apparent contradiction to the Le Chatelier principle is observed [9, 10], and discovery of hitherto unnoticed thermodynamic identities [10]. The most important finding

Reprint requests to Prof. I. Nagypál.

0932-0784 / 96 / 1000-1079 \$ 06.00 © – Verlag der Zeitschrift für Naturforschung, D-72072 Tübingen



Dieses Werk wurde im Jahr 2013 vom Verlag Zeitschrift für Naturforschung in Zusammenarbeit mit der Max-Planck-Gesellschaft zur Förderung der Wissenschaften e.V. digitalisiert und unter folgender Lizenz veröffentlicht: Creative Commons Namensnennung-Keine Bearbeitung 3.0 Deutschland Lizenz.

Zum 01.01.2015 ist eine Anpassung der Lizenzbedingungen (Entfall der Creative Commons Lizenzbedingung „Keine Bearbeitung“) beabsichtigt, um eine Nachnutzung auch im Rahmen zukünftiger wissenschaftlicher Nutzungsformen zu ermöglichen.

This work has been digitalized and published in 2013 by Verlag Zeitschrift für Naturforschung in cooperation with the Max Planck Society for the Advancement of Science under a Creative Commons Attribution-NoDerivs 3.0 Germany License.

On 01.01.2015 it is planned to change the License Conditions (the removal of the Creative Commons License condition “no derivative works”). This is to allow reuse in the area of future scientific usage.

obtained is that every sensitivity coefficient in a chemical equilibrium system may be, in a natural way, partitioned into terms, each being associated with either an individual RER or a pair thereof [9, 10, 11]. Further work along these lines revealed that all these results have a common origin in a third, novel, formulation of the change of Gibbs energy. The aim of this note is to present this new formulation and to summarize its main advantages relative to (1) and (2).

At this early point we wish to make clear that we are *not* offering a (new) method suitable for numerical calculations in chemical thermodynamics. Our approach, as we believe, provides certain novel concepts useful for understanding and rationalizing the (often very complicated) behavior of multiple-equilibrium systems.

### Mathematical Considerations

Consider a closed system in which  $n$  species  $B_1, B_2, \dots, B_n$  interact in accordance with the following set of stoichiometrically independent reactions:

$$\begin{aligned} \nu_{11}B_1 + \nu_{12}B_2 + \dots + \nu_{1n}B_n &= 0, \\ \nu_{21}B_1 + \nu_{22}B_2 + \dots + \nu_{2n}B_n &= 0, \\ &\vdots \\ \nu_{m1}B_1 + \nu_{m2}B_2 + \dots + \nu_{mn}B_n &= 0, \end{aligned} \quad (5)$$

where  $\nu_{ij}$  are the stoichiometric numbers, being negative for reactants, positive for products and zero for species not participating in the given SIR.

Each of these reactions is characterized by its extent  $\xi_j$  and affinity  $A_j$ , defined as [5]

$$dn_s = \sum_{j=1}^m \nu_{js} d\xi_j; \quad s = 1, 2, \dots, n, \quad (6)$$

$$A_j = - \sum_{s=1}^n \nu_{js} \mu_s; \quad j = 1, 2, \dots, m, \quad (7)$$

where  $n_s$  is the amount (number of moles) of species  $B_s$ .

At  $T, P = \text{const.}$  the Gibbs energy may be regarded either as a function of the extents of reactions  $\xi_1, \xi_2, \dots, \xi_m$  or as a function of the amounts

of species  $n_1, n_2, \dots, n_n$ . Thus, we can define two Hessian matrices:

$$\mathbf{G} = \|G_{ij}\|; \quad G_{ij} = \frac{1}{RT} \left( \frac{\partial^2 G}{\partial \xi_i \partial \xi_j} \right), \quad (8)$$

$$i, j = 1, 2, \dots, m,$$

$$\mathbf{R} = \|R_{ij}\|; \quad R_{ij} = \frac{1}{RT} \left( \frac{\partial^2 G}{\partial n_i \partial n_j} \right), \quad (9)$$

$$i, j = 1, 2, \dots, n.$$

These are related via

$$\mathbf{G} = \nu \mathbf{R} \nu^t, \quad (10)$$

i. e.,

$$G_{ij} = \sum_{r=1}^n \sum_{s=1}^n \nu_{ir} \nu_{js} R_{rs}, \quad (11)$$

where superscript  $t$  denotes transposition. Recall that  $G_{ij} = G_{ji}$  and  $R_{ij} = R_{ji}$ , i. e.,  $\mathbf{G} = \mathbf{G}^t$  and  $\mathbf{R} = \mathbf{R}^t$ . The determinant of the Hessian matrix  $\mathbf{G}$  is denoted by  $\Delta$  and will be referred to as the Hessian determinant. It is necessarily positive-valued [5].

At  $T, P = \text{const.}$ , the affinities are functions only of the extents of reactions. Therefore

$$dA_i = \sum_{j=1}^m \left( \frac{\partial A_i}{\partial \xi_j} \right) d\xi_j; \quad i = 1, 2, \dots, m. \quad (12)$$

By taking into account that

$$- \left( \frac{\partial A_r}{\partial \xi_s} \right) = \frac{\partial^2 G}{\partial \xi_r \partial \xi_s} = RT G_{rs},$$

(12) is rewritten as

$$- \frac{1}{RT} dA_i = \sum_{j=1}^m G_{ij} d\xi_j; \quad i = 1, 2, \dots, m. \quad (13)$$

The given set of independent variables

$d\xi_1, d\xi_2, \dots, d\xi_m$  can be transformed into the set of  $dA_1, dA_2, \dots, dA_m$ , as the Hessian determinant is different from zero:

$$d\xi_r = - \frac{1}{RT} \frac{\Delta_r}{\Delta}, \quad (14)$$

where

$$\Delta_r = \begin{vmatrix} G_{11} & G_{12} & \cdots & G_{1,r-1} & dA_1 & G_{1,r+1} & \cdots & G_{1m} \\ G_{21} & G_{22} & \cdots & G_{2,r-1} & dA_2 & G_{2,r+1} & \cdots & G_{2m} \\ \vdots & \vdots & & \vdots & \vdots & \vdots & & \vdots \\ G_{m1} & G_{m2} & \cdots & G_{m,r-1} & dA_m & G_{m,r+1} & \cdots & G_{mm} \end{vmatrix}. \quad (15)$$

Thus, for the change of Gibbs energy:

$$dG_{T,P} = \frac{1}{RT\Delta} \sum_{r=1}^m A_r \Delta_r \quad (16)$$

Equation (16) may easily be transformed into

$$dG_{T,P} = \sum_{r=1}^m \sum_{s=1}^m L_{rs} A_r dA_s, \quad (17)$$

where

$$L_{rs} = \frac{1}{RT\Delta} (-1)^{r+s} D_{rs} \quad (18)$$

and where  $D_{rs}$  is the minor of the determinant  $\Delta_r$ , (15), obtained by deleting its  $r$ -th column and  $s$ -th row.

The response reactions are defined by the stoichiometric equation [11]:

$$\sum_{k=1}^n D_k([i]) B_k = 0,$$

where

$$D_k([i]) = \begin{vmatrix} \nu_{1,i_1} & \nu_{1,i_2} & \cdots & \nu_{1,i_{m-1}} & \nu_{1k} \\ \nu_{2,i_1} & \nu_{2,i_2} & \cdots & \nu_{2,i_{m-1}} & \nu_{2k} \\ \vdots & \vdots & & \vdots & \vdots \\ \nu_{m,i_1} & \nu_{m,i_2} & \cdots & \nu_{m,i_{m-1}} & \nu_{mk} \end{vmatrix}. \quad (19)$$

The indices  $i_1, i_2, \dots, i_{m-1}$  satisfy the condition  $1 \leq i_1 < i_2 < \dots < i_{m-1} \leq n$  and pertain to the respective columns of the stoichiometric matrix, i. e., to the species  $B_{i_1}, B_{i_2}, \dots, B_{i_{m-1}}$ . Hence, a particular response reaction is determined by a choice of  $m-1$  species form a total of  $n$ . Therefore the number of response reactions is  $r = \binom{n}{m-1}$ . They are not all independent, but they have the remarkable property of being unique, i. e., being independent of the SIRs they are derived from [12].

For the sake of brevity, the  $(m-1)$ -tuple of integers  $i_1, i_2, \dots, i_{m-1}$ , satisfying the above specified conditions, will be denoted by  $[i]$ . In harmony with this,  $[j]$  symbolizes the numbers  $j_1, j_2, \dots, j_{m-1}$ , for which  $1 \leq j_1 < j_2 < \dots < j_{m-1} \leq n$ .

It can be shown [7] that the affinity of the  $[i]$ -th response reaction is given by

$$A([i]) = \begin{vmatrix} \nu_{1,i_1} & \nu_{1,i_2} & \cdots & \nu_{1,i_{m-1}} & A_1 \\ \nu_{2,i_1} & \nu_{2,i_2} & \cdots & \nu_{2,i_{m-1}} & A_2 \\ \vdots & \vdots & & \vdots & \vdots \\ \nu_{m,i_1} & \nu_{m,i_2} & \cdots & \nu_{m,i_{m-1}} & A_m \end{vmatrix}, \quad (20)$$

and that an analogous relation holds for its differential:

$$dA([i]) = \begin{vmatrix} \nu_{1,i_1} & \nu_{1,i_2} & \cdots & \nu_{1,i_{m-1}} & dA_1 \\ \nu_{2,i_1} & \nu_{2,i_2} & \cdots & \nu_{2,i_{m-1}} & dA_2 \\ \vdots & \vdots & & \vdots & \vdots \\ \nu_{m,i_1} & \nu_{m,i_2} & \cdots & \nu_{m,i_{m-1}} & dA_m \end{vmatrix}. \quad (21)$$

Expansion of the latter two determinants with respect to their  $m$ -th columns yields

$$A([i]) = \sum_{r=1}^m (-1)^{r+m} A_r d_{rm}([i]), \quad (22)$$

$$dA([j]) = \sum_{s=1}^m (-1)^{s+m} dA_s d_{sm}([j]), \quad (23)$$

where  $d_{rm}([i])$  and  $d_{sm}([j])$  are the respective minors. Applying the Binet-Cauchy formula [15] to the minor  $D_{rs}$  of the determinant  $\Delta_r$ , (15), and by taking into account (10) we arrive at

$$D_{rs} = \sum_{[i]} \sum_{[j]} d_{rm}([i]) R([i], [j]) d_{sm}([j]), \quad (24)$$

where

$$R([i], [j]) = \begin{vmatrix} R_{i_1,j_1} & R_{i_1,j_2} & \cdots & R_{i_1,j_{m-1}} \\ R_{i_2,j_1} & R_{i_2,j_2} & \cdots & R_{i_2,j_{m-1}} \\ \vdots & \vdots & & \vdots \\ R_{i_{m-1},j_1} & R_{i_{m-1},j_2} & \cdots & R_{i_{m-1},j_{m-1}} \end{vmatrix}. \quad (25)$$

## The Main Result

Substitution of (24) into (17) and taking into account (22) and (23) leads to the main result of the present communication:

$$dG_{(T,P)} = \sum_{[i]} \sum_{[j]} \gamma([i], [j]) A([i]) dA([j]), \quad (26)$$

where  $\gamma([i], [j])$  is a quantity which accounts for coupling between RERs:

$$\gamma([i], [j]) = \frac{1}{RT} \frac{\mathbf{R}([i], [j])}{\Delta}$$

The summation in (26) goes over all RERs and pairs thereof.

Differentiation of (26) with respect to time gives

$$\left( \frac{dG}{dt} \right)_{T,P} = \sum_{[i]} \sum_{[j]} \gamma([i], [j]) A([i]) \frac{dA([j])}{dt},$$

and because the Gibbs energy is a monotonously decreasing function of time, the De Donder theorem takes the form

$$\sum_{[i]} \sum_{[j]} \gamma([i], [j]) A([i]) \frac{dA([j])}{dt} \leq 0. \quad (27)$$

At equilibrium:

$$A([i]) = 0, \quad \frac{dA([j])}{dt} = 0. \quad (28)$$

## Discussion

The above considerations show that there exists a unique stoichiometric representation in the chemical thermodynamics of multiple reactions. In other words, the arbitrary SIRs can always be transformed into the same, therefore unique, RERs.

The transformation of the fundamental equations of chemical thermodynamics, from a SIR-basis to the RERs, envisages new, hitherto unnoticed, features of these equations. This has two consequences. First, the controversial concept of thermodynamic coupling may be interpreted in a new qualitative and quantitative manner. In terms of RERs the coupling appears in a natural way and is given explicitly by  $\gamma([i], [j])$ . Second, the substitution of extents of reactions as independent variables by affinities, implies that in nonequilibrium thermodynamics the role of flux is played by the rate of change of affinities, instead by the rate of change of extents of reactions. By this, inadequacies due to different transformation rules for the forces and fluxes in nonequilibrium systems [4] are automatically eliminated.

An important advantage of the present approach (in terms of RERs), compared to the standard approach (in terms of SIRs), is that the sensitivity coefficients, characterizing the response of an equilibrium system to the change of different parameters governing its position, may be decomposed into sums of terms, uniquely assigned to individual RERs, [8] - [11], [13]. The formulation put forward in this letter enables the use of the concept of RERs in nonequilibrium thermodynamics as well.

We have presented here only a brief summary of the applications of RERs in chemical thermodynamics, putting emphasis on the Gibbs energy. Evidently, RERs can be used in connection with other thermodynamic potential functions, and with other important thermodynamic quantities, such as first derivatives, etc. Work along the line of building up a complete set of thermodynamic relations based on this approach is in progress.

## Acknowledgement

This work was supported by the National Science Foundation of Hungary (OTKA, No. 4207). One author (I. G.) thanks the Mathematical Institute in Belgrade for financial support.

- [1] J. W. Gibbs, The Scientific Papers of J. Willard Gibbs. Vol. 1., Thermodynamics, New York 1903.
- [2] T. De Donder and P. Van Rysselberghe, Thermodynamic Theory of Affinity. University Press, Stanford 1936.
- [3] F. O. Koenig, F. H. Horne, and D. M. Mohilner, J. Amer. Chem. Soc. **83**, 1029 (1961).
- [4] J. Keizer, J. Theor. Biol. **49**, 323 (1975).
- [5] I. Prigogine and R. Defay, Chemical Thermodynamics. Longmans, London 1954.
- [6] I. Prigogine, Introduction to Thermodynamics of Irreversible Processes. Interscience, New York 1961.
- [7] I. Fishtik, I. Nagypál, and I. Gutman, J. Chem. Soc. Faraday Trans. **90**, 3245 (1994).

- [8] I. Gutman, I. Fishtik, and I. Nagypál, *J. Math. Chem.* **16**, 229 (1994).
- [9] I. Fishtik, I. Nagypál, and I. Gutman, *J. Chem. Soc. Faraday Trans.* **91**, 259 (1995).
- [10] I. Fishtik, I. Nagypál, and I. Gutman, *J. Chem. Soc. Faraday Trans.* **91**, 1325 (1995).
- [11] I. Fishtik, I. Nagypál, and I. Gutman, *J. Chem. Phys.* **103**, 7545 (1995).
- [12] I. Gutman and I. Nagypál, *J. Math. Chem.*, in press.
- [13] I. Gutman, I. Nagypál, and I. Fishtik, *J. Math. Chem.* **18**, 73 (1995).
- [14] I. Nagypál and M. T. Beck, *J. Phys. Chem.* **84**, 722 (1980).
- [15] R. F. Gantmaher, *Theory of Matrices*. Vol.1, Chelsea, New York 1960.