

# General thermodynamic identities for sensitivity coefficients

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Expressions are obtained for the sensitivity coefficients  $\partial n_i / \partial Y$  of the equilibrium state of a homogeneous multicomponent system in which chemical reactions occur, and in which ideal behavior of the components is *not* assumed;  $n_i$  is the equilibrium amount of the  $i$ th chemical species, and  $Y$  is a parameter influencing the equilibrium. These thermodynamic identities represent generalizations of the results of the same kind, recently reported for systems with ideal behavior [I. Gutman, I. Fishtik and I. Nagypál, *J. Math. Chem.* 16 (1994) 229]. Also in the most general case,  $\partial n_i / \partial Y$  is found to be equal to the sum of contributions originating from certain special equilibria, previously named as Hessian response reactions.

## 1. Introduction

In a recent paper [1] we reported thermodynamic identities for the sensitivity coefficients of equilibrium systems in which all the components were assumed to obey ideal behavior. We now extend these results so as to hold for arbitrary homogeneous chemically reacting systems at equilibrium.

The notation used in this paper is the same as in [1], and therefore its details will not be specified here once again. The system considered consists of  $n$  distinct species  $A_1, A_2, \dots, A_n$  whose chemical conversion is described by means of  $m$  (stoichiometrically independent) chemical equations:

$$\nu_{r1}A_1 + \nu_{r2}A_2 + \dots + \nu_{rn}A_n = 0, \quad r = 1, 2, \dots, m. \quad (1)$$

The system is homogeneous and is at equilibrium. The equilibrium amount (number of moles) of the species  $A_i$  is denoted by  $n_i$  whereas its initial amount is  $n_{i0}$ ,  $i = 1, 2, \dots, n$ . The total number of moles at equilibrium is  $n_t$ ; in the general case  $n_t \geq n_1 + n_2 + \dots + n_n$ , because some additional substances, not participating in the reactions (1), e.g. a solvent, may be present in the system.

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We are concerned with the response of the equilibrium composition to the change of a certain variable  $Y$  (which may be temperature, pressure, initial amount of a species, etc.). This response is expressed by means of the so-called sensitivity coefficients  $\partial n_i / \partial Y$ ,  $i = 1, 2, \dots, n$ .

The extent of the  $r$ th reaction (1) at equilibrium is denoted by  $\xi_r$ ,  $r = 1, 2, \dots, m$ , and the Gibbs energy  $G$  of the system is viewed as a function of the variables  $\xi_1, \xi_2, \dots, \xi_m$ . We define [1]

$$G_{rs} = \frac{1}{RT} \partial^2 G / \partial \xi_r \partial \xi_s. \quad (2)$$

One of the starting points in our consideration is relation (3):

$$\partial n_k / \partial Y = \delta + \frac{1}{\Delta} \sum_{j=1}^m \nu_{jk} \Delta_j, \quad (3)$$

in which  $\Delta$  and  $\Delta_j$  are the determinants

$$\Delta = \begin{vmatrix} G_{11} & G_{12} & \dots & G_{1m} \\ G_{21} & G_{22} & \dots & G_{2m} \\ \dots & \dots & \dots & \dots \\ G_{m1} & G_{m2} & \dots & G_{mm} \end{vmatrix} \quad (4)$$

and

$$\Delta_j = \begin{vmatrix} G_{11} & G_{12} & \dots & G_{1,j-1} & X_1 & G_{1,j+1} & \dots & G_{1m} \\ G_{21} & G_{22} & \dots & G_{2,j-1} & X_2 & G_{2,j+1} & \dots & G_{2m} \\ \dots & \dots & \dots & \dots & \dots & \dots & \dots & \dots \\ G_{m1} & G_{m2} & \dots & G_{m,j-1} & X_m & G_{m,j+1} & \dots & G_{mm} \end{vmatrix}. \quad (5)$$

Further,  $\delta = 1$  if  $Y = n_{k0}$  and  $\delta = 0$  otherwise. The quantities  $X_1, X_2, \dots, X_m$ , occurring in  $\Delta_j$ , depend on the actual choice of the variable  $Y$ ;  $X_r$  is associated with the  $r$ th reaction (1). More details of this matter can be found in [1–3]. Recall that  $\Delta$  is the Hessian determinant of the system considered.

Formula (3) is a generally valid thermodynamic identity; its derivation can be found in [1] or [3].

Let  $\mu_i$  be the chemical potential of the  $i$ th species. Then

$$G = \sum_{i=1}^n n_i \mu_i$$

and

$$\partial G / \partial \xi_r = \sum_{i=1}^n \mu_i (\partial n_i / \partial \xi_r) + \sum_{i=1}^n n_i (\partial \mu_i / \partial \xi_r). \quad (6)$$

Because of the Gibbs–Duhem equation, the second sum on the right-hand side of (6) is zero. Besides, because of the mass-balance conditions

$$n_i = n_{i0} + \sum_{r=1}^m \nu_{ri} \xi_r, \quad i = 1, 2, \dots, n,$$

one has  $\partial n_i / \partial \xi_r = \nu_{ri}$ . This implies

$$\partial G / \partial \xi_r = \sum_{i=1}^n \nu_{ri} \mu_i$$

and, finally,

$$\partial^2 G / \partial \xi_r \partial \xi_s = \sum_{i=1}^n \nu_{ri} (\partial \mu_i / \partial \xi_s). \quad (7)$$

Formula (7) can be written in a more compact form by introducing the auxiliary quantities

$$\mu_{si} \equiv \frac{1}{RT} (\partial \mu_i / \partial \xi_s).$$

Then in view of (2),

$$G_{rs} = \sum_{i=1}^n \nu_{ri} \mu_{si}. \quad (8)$$

Observe that because of  $G_{rs} = G_{sr}$ , it holds that

$$\sum_{i=1}^n \nu_{ri} \mu_{si} = \sum_{i=1}^n \mu_{ri} \nu_{si}. \quad (9)$$

Formula (8) is also a generally valid thermodynamic identity [2,3]. It will serve as the other starting point in our approach to sensitivity coefficients.

## 2. The main results

As before [1] we use the short-hand notation  $D(i_1, \dots, i_{m-1}, k)$  and  $D(i_1, \dots, i_{m-1}, X)$  for the two determinants below:

$$D(i_1, i_2, \dots, i_{m-1}, k) = \begin{vmatrix} \nu_{1,i_1} & \nu_{1,i_2} & \dots & \nu_{1,i_{m-1}} & \nu_{1,k} \\ \nu_{2,i_1} & \nu_{2,i_2} & \dots & \nu_{2,i_{m-1}} & \nu_{2,k} \\ \vdots & \vdots & & \vdots & \vdots \\ \nu_{m,i_1} & \nu_{m,i_2} & \dots & \nu_{m,i_{m-1}} & \nu_{m,k} \end{vmatrix},$$

$$D(i_1, i_2, \dots, i_{m-1}, X) = \begin{vmatrix} \nu_{1,i_1} & \nu_{1,i_2} & \dots & \nu_{1,i_{m-1}} & X_1 \\ \nu_{2,i_1} & \nu_{2,i_2} & \dots & \nu_{2,i_{m-1}} & X_2 \\ \vdots & \vdots & & \vdots & \vdots \\ \nu_{m,i_1} & \nu_{m,i_2} & \dots & \nu_{m,i_{m-1}} & X_m \end{vmatrix}.$$

In addition to this, we introduce two further abbreviations –  $T(i_1, \dots, i_{m-1}, k)$  and  $T(i_1, \dots, i_{m-1}, X)$ :

$$T(i_1, i_2, \dots, i_{m-1}, k) = \begin{vmatrix} \mu_{1,i_1} & \mu_{1,i_2} & \dots & \mu_{1,i_{m-1}} & \nu_{1,k} \\ \mu_{2,i_1} & \mu_{2,i_2} & \dots & \mu_{2,i_{m-1}} & \nu_{2,k} \\ \vdots & \vdots & & \vdots & \vdots \\ \mu_{m,i_1} & \mu_{m,i_2} & \dots & \mu_{m,i_{m-1}} & \nu_{m,k} \end{vmatrix}, \quad (10)$$

$$T(i_1, i_2, \dots, i_{m-1}, X) = \begin{vmatrix} \mu_{1,i_1} & \mu_{1,i_2} & \dots & \mu_{1,i_{m-1}} & X_1 \\ \mu_{2,i_1} & \mu_{2,i_2} & \dots & \mu_{2,i_{m-1}} & X_2 \\ \vdots & \vdots & & \vdots & \vdots \\ \mu_{m,i_1} & \mu_{m,i_2} & \dots & \mu_{m,i_{m-1}} & X_m \end{vmatrix}. \quad (11)$$

In the special case when  $X_r = \mu_{rk}$ ,  $r = 1, 2, \dots, m$ , the determinant (11) is written as  $T(i_1, i_2, \dots, i_{m-1}, \mu_k)$ .

Observe that the determinants  $T(i_1, \dots, i_{m-1}, k)$  and  $T(i_1, \dots, i_{m-1}, X)$  are obtained by changing the symbols  $\nu$  into  $\mu$  in the first  $m - 1$  columns of  $D(i_1, \dots, i_{m-1}, k)$  and  $D(i_1, \dots, i_{m-1}, X)$ , respectively.

Our main results can now be formulated as follows.

### Result 1

$$\Delta = \frac{1}{m} \sum_{1 \leq i_1 < i_2 < \dots < i_{m-1} \leq n} \sum_{k=1}^n D(i_1, i_2, \dots, i_{m-1}, k) T(i_1, i_2, \dots, i_{m-1}, \mu_k). \quad (12)$$

### Result 2

$$\partial n_k / \partial Y = \delta + \frac{1}{\Delta} \sum_{1 \leq i_1 < i_2 < \dots < i_{m-1} \leq n} D(i_1, i_2, \dots, i_{m-1}, k) T(i_1, i_2, \dots, i_{m-1}, X), \quad (13)$$

$$\partial n_k / \partial Y = \delta + \frac{1}{\Delta} \sum_{1 \leq i_1 < i_2 < \dots < i_{m-1} \leq n} T(i_1, i_2, \dots, i_{m-1}, k) D(i_1, i_2, \dots, i_{m-1}, X). \quad (14)$$

To the authors' best knowledge, none of the thermodynamic identities (12)–(14) was previously reported.

### 3. Proof of formula (12)

Introduce the matrices  $\nu = \|\nu_{ri}\|$  and  $\mu = \|\mu_{ri}\|$ , both of dimension  $m \times n$  and thus rewrite eq. (8) as

$$G_{rs} = (\nu\mu^t)_{rs}, \tag{15}$$

where the superscript  $t$  indicates transposition. Bearing in mind (15), we expand the determinant  $\Delta$ , eq. (4), by means of the Binet–Cauchy formula to obtain

$$\Delta = \sum_{1 \leq i_1 < i_2 < \dots < i_m \leq n} \begin{vmatrix} \nu_{1,i_1} & \nu_{1,i_2} & \dots & \nu_{1,i_{m-1}} & \nu_{1,i_m} \\ \nu_{2,i_1} & \nu_{2,i_2} & \dots & \nu_{2,i_{m-1}} & \nu_{2,i_m} \\ \vdots & \vdots & & \vdots & \vdots \\ \nu_{m,i_1} & \nu_{m,i_2} & \dots & \nu_{m,i_{m-1}} & \nu_{m,i_m} \end{vmatrix} \times \begin{vmatrix} \mu_{1,i_1} & \mu_{1,i_2} & \dots & \mu_{1,i_{m-1}} & \mu_{1,i_m} \\ \mu_{2,i_1} & \mu_{2,i_2} & \dots & \mu_{2,i_{m-1}} & \mu_{2,i_m} \\ \vdots & \vdots & & \vdots & \vdots \\ \mu_{m,i_1} & \mu_{m,i_2} & \dots & \mu_{m,i_{m-1}} & \mu_{m,i_m} \end{vmatrix},$$

i.e.

$$\Delta = \sum_{1 \leq i_1 < i_2 < \dots < i_m \leq n} D(i_1, i_2, \dots, i_{m-1}, i_m) T(i_1, i_2, \dots, i_{m-1}, \mu_{i_m}). \tag{16}$$

Equation (12) follows now from the fact that since the summands in (16) are products of two determinants of order  $m$ ,

$$\sum_{1 \leq i_1 < i_2 < \dots < i_m \leq n} = \frac{1}{m} \sum_{1 \leq i_1 < i_2 < \dots < i_{m-1} \leq n} \sum_{k=1}^n.$$

### 4. Proof of formula (14)

We start with formula (3) and expand the determinant  $\Delta_j$  with respect to its  $j$ th column:

$$\partial n_k / \partial Y = \delta + \frac{1}{\Delta} \sum_{j=1}^m \nu_{jk} \sum_{i=1}^m (-1)^{i+j} X_i \Delta(i|j). \tag{17}$$

Here and later  $\Delta(i|j)$  denotes the minor, obtained from  $\Delta$  by deleting its  $i$ th row and  $j$ th column.

We next employ eq. (8) and expand  $\Delta(i|j)$  with respect to all its  $m - 1$  columns. This expansion technique was already used in [1] and there it was explained in due detail. The final result is

$$\Delta(i|j) = \sum_{i_1=1}^n \sum_{i_2=1}^n \cdots \sum_{i_{m-1}=1}^n \mu_{1,i_1} \mu_{2,i_2} \cdots \mu_{j-1,i_{j-1}} \mu_{j+1,i_j} \cdots \mu_{m,i_{m-1}} \times D(i_1, i_2, \dots, i_{m-1}, i_m)(i|m). \quad (18)$$

In harmony with the previously introduced notation,  $D(i_1, i_2, \dots, i_{m-1}, i_m)(i|m)$  stands for the minor of  $D(i_1, i_2, \dots, i_{m-1}, i_m)$ , obtained by deleting its  $i$ th row and  $m$ th column.

Whenever at least two among the indices  $i_1, i_2, \dots, i_{m-1}$  are equal, then  $D(i_1, i_2, \dots, i_{m-1}, i_m)(i|m) = 0$ . Consequently, the only non-zero contributions to the right-hand side of (18) come from summands in which all the indices  $i_1, i_2, \dots, i_{m-1}$  are mutually distinct.

Taking the above into account, we can follow a reasoning fully analogous to what in [1] was used to deduce eq. (33) from eq. (30). By means of it, eq. (18) is transformed into (19). The details of these (otherwise quite perplexed) algebraic manipulations can be found in [1] and are not repeated here once again. We thus arrive at

$$\Delta(i|j) = \sum_{i_1 < i_2 < \dots < i_{m-1}} T(i_1, i_2, \dots, i_{m-1}, i_m)(j|m) D(i_1, i_2, \dots, i_{m-1}, i_m)(i|m). \quad (19)$$

Substituting (19) back into (17) and making a few pertinent rearrangements, we obtain

$$\begin{aligned} \partial n_k / \partial Y = & \delta + \frac{1}{\Delta} \sum_{i_1 < i_2 < \dots < i_{m-1}} \left[ \sum_{j=1}^m (-1)^{m+j} \nu_{jk} T(i_1, i_2, \dots, i_{m-1}, i_m)(j|m) \right] \\ & \times \left[ \sum_{i=1}^m (-1)^{m+i} X_i D(i_1, i_2, \dots, i_{m-1}, i_m)(i|m) \right]. \end{aligned} \quad (20)$$

Equation (14) is now straightforwardly obtained from (20) by observing that the Laplace expansions of  $T(i_1, i_2, \dots, i_{m-1}, k)$  and  $D(i_1, i_2, \dots, i_{m-1}, X)$ , with respect to the  $m$ th column, are just

$$T(i_1, i_2, \dots, i_{m-1}, k) = \sum_{j=1}^m (-1)^{m+j} \nu_{jk} T(i_1, i_2, \dots, i_{m-1}, i_m)(j|m),$$

$$D(i_1, i_2, \dots, i_{m-1}, X) = \sum_{i=1}^m (-1)^{m+i} X_i D(i_1, i_2, \dots, i_{m-1}, i_m)(i|m).$$

## 5. Proof of formula (13)

Formula (13) could have been deduced in a fully analogous manner to that used for identity (14). However, there is a much faster route towards (13).

Equation (8) possesses a certain peculiar symmetry. Namely, eq. (8) is invariant on the exchange of the characters  $\nu$  and  $\mu$  (which, on the other hand, pertain to completely different physico-chemical quantities). This property is best seen from eq. (9).

Now, the  $\nu/\mu$ -invariance will be inherited by all formulas deduced from eq. (8). In particular, it is permitted to modify eq. (14) so that all symbols  $\mu$  occurring in the first  $m - 1$  columns of  $T(i_1, i_2, \dots, i_{m-1}, k)$  are turned into  $\nu$ , and all symbols  $\nu$  occurring in the first  $m - 1$  columns of  $D(i_1, i_2, \dots, i_{m-1}, X)$  are switched into  $\mu$ . This yields eq. (13).

## 6. Concerning the interpretation of the identities (13) and (14)

In our previous researches on sensitivity analysis [1,4,5] (which all were devoted to systems with ideal behavior), we introduced the concept of Hessian response reactions, namely of equilibria of the form

$$\nu_1 A_1 + \nu_2 A_2 + \dots + \nu_n A_n = 0 \quad (21)$$

for which  $\nu_i = D(i_1, i_2, \dots, i_{m-1}, i)$ ,  $i = 1, 2, \dots, n$ .

Because (21) is in fact an equilibrium, the name "reaction" for it is somewhat misleading. Therefore, in what follows, instead of "Hessian response reaction" we shall use the more appropriate term "*Hessian response equilibrium*".

Each selection of  $m - 1$  distinct indices  $i_1, i_2, \dots, i_{m-1}$ , such that  $1 \leq i_1 < i_2 < \dots < i_{m-1} \leq n$ , defines a particular Hessian equilibrium  $\mathcal{H}(i_1, i_2, \dots, i_{m-1})$ . More details on Hessian equilibria are found elsewhere [1,4].

From the form of eqs. (13) and (14) the following interpretation is immediate: According to both eqs. (13) and (14), the sensitivity coefficient  $\partial n_k / \partial Y$  is equal to the sum of contributions coming from Hessian equilibria.

(a) According to eq. (13), the contribution of  $\mathcal{H}(i_1, \dots, i_{m-1})$  is equal to  $(1/\Delta)D(i_1, \dots, i_{m-1}, k)T(i_1, \dots, i_{m-1}, X)$ , where  $D(i_1, \dots, i_{m-1}, k)$  is recognized as the stoichiometric coefficient of the  $k$ th species in the respective Hessian equilibrium.

(b) According to eq. (14), the contribution of  $\mathcal{H}(i_1, \dots, i_{m-1})$  is equal to  $(1/\Delta)T(i_1, \dots, i_{m-1}, k)D(i_1, \dots, i_{m-1}, X)$ , where  $D(i_1, \dots, i_{m-1}, X)$  is recognized as the change of the quantity  $X$  in the respective Hessian equilibrium.

As seen from the identity (12), the Hessian determinant  $\Delta$  is also expressible in the form of a sum of contributions associated with Hessian equilibria.

What remains obscure in (13) and (14) is the possible thermodynamic interpretation of the terms  $T(i_1, \dots, i_{m-1}, k)$  and  $T(i_1, \dots, i_{m-1}, X)$ . An additional difficulty

is that the expressions  $(1/\Delta)D(i_1, \dots, i_{m-1}, k)T(i_1, \dots, i_{m-1}, X)$  and  $(1/\Delta)T(i_1, \dots, i_{m-1}, k)D(i_1, \dots, i_{m-1}, X)$ , both associated with the same Hessian equilibrium  $\mathcal{H}(i_1, \dots, i_{m-1})$  may have different numerical values. We intend to resolve some of these problems in the future [6].

## 7. A special case: Systems with ideal behavior

Special cases of the formulas (12)–(14) for systems in which all species exhibit an ideal behavior were reported previously [1,5]. In order to obtain these expressions one has to use the specific form which the quantities  $G_{rs}$  and  $\mu_{ri}$  attain in systems with ideal behavior, namely [2,3]

$$G_{rs} = \sum_{i=1}^n \frac{1}{n_i} \nu_{ri} \nu_{si} - \frac{1}{n_t} \left( \sum_{i=1}^n \nu_{ri} \right) \left( \sum_{i=1}^n \nu_{si} \right) \quad (22)$$

and

$$\mu_{ri} = \frac{1}{n_i} \nu_{ri} - \frac{1}{n_t} \sum_{i=1}^n \nu_{ri}. \quad (23)$$

By combining (22) with (5) and (17) one obtains [1]<sup>2</sup>

$$\begin{aligned} \partial n_k / \partial Y = \delta + \frac{1}{\Delta} \left[ \sum_{i_1 < i_2 < \dots < i_{m-1}} \frac{D(i_1, i_2, \dots, i_{m-1}, k) D(i_1, i_2, \dots, i_{m-1}, X)}{n_{i_1} n_{i_2} \dots n_{i_{m-1}}} \right. \\ \left. - \frac{1}{n_t} \sum_{i_1 < i_2 < \dots < i_{m-2}} \frac{D(i_1, i_2, \dots, i_{m-2}, \Delta\nu, k) D(i_1, i_2, \dots, i_{m-2}, \Delta\nu, X)}{n_{i_1} n_{i_2} \dots n_{i_{m-2}}} \right], \end{aligned} \quad (24)$$

where

$$D(i_1, i_2, \dots, i_{m-2}, \Delta\nu, k) = \sum_{i=1}^n D(i_1, i_2, \dots, i_{m-2}, i, k),$$

$$D(i_1, i_2, \dots, i_{m-2}, \Delta\nu, X) = \sum_{i=1}^n D(i_1, i_2, \dots, i_{m-2}, i, X).$$

The above formula (24) is the same as eq. (13) in [1]<sup>2</sup>. Details of the sensitivity analysis of ideal systems, based on eq. (24) can be found elsewhere [1,5]. In the spirit

<sup>2</sup> A small, but awkward sign error occurred in eq. (13) in [1]: the sign between the two summations on the right-hand side of (13) is not plus but minus (as in the present eq. (24)). The same error should be eliminated also from eqs. (16), (17), (28) and from the formula given at the end of section 6 of [1]. In eq. (35) in [1],  $(-1)^{h+l-1}$  should be replaced by  $(-1)^{h+l}$ .



of eq. (24) the sensitivity coefficients are presented as sums of contributions coming from Hessian and non-Hessian response equilibria,  $\mathcal{H}(i_1, i_2, \dots, i_{m-1})$  and  $\mathcal{N}(i_1, i_2, \dots, i_{m-2})$ , respectively [1,5]. Recall that  $\mathcal{N}(i_1, i_2, \dots, i_{m-2})$  is an equilibrium of the form (21), for which  $\nu_i = \sum_{k=1}^n D(i_1, i_2, \dots, i_{m-2}, k, i)$ ,  $i = 1, 2, \dots, n$  [1].

Another way to arrive at the ideal-behavior special cases of eqs. (12)–(14) is to substitute into them formula (23). From (12)–(14) is immediately seen that the only terms which have to be (can be) simplified are the determinants  $T(i_1, i_2, \dots, i_{m-1}, \mu_k)$ ,  $T(i_1, i_2, \dots, i_{m-1}, k)$  and  $T(i_1, i_2, \dots, i_{m-1}, X)$ . A straightforward calculation yields

$$T(i_1, i_2, \dots, i_{m-1}, \Omega) = \begin{vmatrix} \nu_{1,i_1} & \nu_{1,i_2} & \dots & \nu_{1,i_{m-1}} & \Delta\nu_1 & \Omega_1 \\ \nu_{2,i_1} & \nu_{2,i_2} & \dots & \nu_{2,i_{m-1}} & \Delta\nu_2 & \Omega_2 \\ \dots & \dots & \dots & \dots & \dots & \dots \\ \nu_{m,i_1} & \nu_{m,i_2} & \dots & \nu_{m,i_{m-1}} & \Delta\nu_m & \Omega_m \\ x_{i_1} & x_{i_2} & \dots & x_{i_{m-1}} & -1 & 0 \end{vmatrix}, \quad (25)$$

where  $\Delta\nu_r = \nu_{r1} + \nu_{r2} + \dots + \nu_{rn}$ ,  $\Omega_r = \mu_{rk}$  or  $\nu_{rk}$  or  $X_r$ ,  $r = 1, 2, \dots, m$ , and  $x_i = n_i/n_i$  is the mole fraction of the species  $A_i$ ,  $i = 1, 2, \dots, n$ .

## 8. Discussion and concluding remarks

In this paper we proved novel general thermodynamic identities for the Hessian determinant, eq. (12), and for the sensitivity coefficients, eqs. (13) and (14). These are proper generalizations of results recently obtained [1,4,5] for systems which behave ideally. Our main finding is that also in the most general case Hessian response equilibria play a significant role in determining the sensitivity coefficients. In particular, it is possible to present both the Hessian determinant and the sensitivity coefficients as sums of increments associated in some way with Hessian equilibria.

When studying the sensitivity coefficients of equilibrium systems with ideal behavior [1,5] we encountered two types of response equilibria: Hessian  $\mathcal{H}(i_1, i_2, \dots, i_{m-1})$  and non-Hessian  $\mathcal{N}(i_1, i_2, \dots, i_{m-2})$ . At first glance it may look surprising that non-Hessian response equilibria do not appear in the thermodynamic formalism developed for the general case. This may give the impression that the general formalism is simpler than its special case for ideal systems; compare, for instance, eqs. (13) and (14) with eq. (24). A detailed analysis reveals that the dependence of the sensitivity coefficients on non-Hessian response equilibria is contained, in a concealed form, in the  $T$ -determinants, and especially in eq. (25). Another approach to the same problem is to present the sensitivity coefficients as sums of contributions coming from pairs of Hessian equilibria [6].

Not all terms occurring in our identities have a straightforward physico-chemical (thermodynamic) interpretation, either in the general case or in the special

case of ideal systems. This, in particular, applies to the  $T$ -determinants, eqs. (10), (11) and (25). Work aimed at a better understanding of the properties of these quantities is in progress [6].

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