

Mathematical foundation of the Hessian response equilibrium concept

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In our previous studies of systems with multiple chemical equilibria we examined sensitivity coefficients $\partial n_k / \partial Y$, where n_k is the equilibrium amount of the k th chemical species, and Y is a parameter influencing the equilibrium. The chemical transformations in the system are described by means of stoichiometrically independent reactions (SIRs). It was shown that the sensitivity coefficients can be expressed in terms of contributions associated with so-called Hessian response equilibria (HEQs). We now prove some fundamental properties of HEQs, among which are the following: 1. The HEQs are independent of the choice of SIRs. 2. The number of linearly independent HEQs is equal to the number of SIRs.

1. Introduction

Consider a system in which chemical reactions occur between n distinct species A_1, A_2, \dots, A_n . Suppose the system reached its equilibrium state (at constant temperature and pressure). Let n_i denote the equilibrium amount of A_k , $k = 1, 2, \dots, n$. Let Y be a parameter whose change affects the equilibrium, i.e., causes n_k to change. The quantity $\partial n_k / \partial Y$ is a *sensitivity coefficient* (of the species A_k with respect to the parameter Y). The part of chemical thermodynamics concerned with sensitivity coefficients is called *sensitivity analysis*.

The chemical conversion of the species A_1, A_2, \dots, A_n is described by means of the relations

$$\left. \begin{aligned} \nu_{11}A_1 + \nu_{12}A_2 + \dots + \nu_{1n}A_n &= 0 \\ \nu_{21}A_1 + \nu_{22}A_2 + \dots + \nu_{2n}A_n &= 0 \\ \dots & \dots \dots \\ \nu_{m1}A_1 + \nu_{m2}A_2 + \dots + \nu_{mn}A_n &= 0 \end{aligned} \right\} \quad (1)$$

which are usually referred to as “reactions” [1]. These relations are required to be stoichiometrically independent, which means that the vectors $(\nu_{j1}, \nu_{j2}, \dots, \nu_{jn})$, $j = 1, 2, \dots, m$, are all linearly independent. Such a linear independence is achieved if the rank of the stoichiometric matrix \mathbf{v}

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$$\mathbf{v} = \begin{pmatrix} \nu_{11} & \nu_{12} & \dots & \nu_{1n} \\ \nu_{21} & \nu_{22} & \dots & \nu_{2n} \\ \dots & & & \\ \nu_{m1} & \nu_{m2} & \dots & \nu_{mn} \end{pmatrix} \quad (2)$$

is equal to m . In what follows eqs. (1) will be said to represent a set of *stoichiometrically independent reactions* (SIRs). Recall that SIRs can be chosen in infinitely many different, but (from the point of view of chemical equilibrium analysis) equivalent ways. In particular, any linear combination of the SIRs (1) is (from such a viewpoint) a stoichiometrically acceptable “chemical reaction”.

Let (3) and (4) be stoichiometric relations between the species A_1, A_2, \dots, A_n :

$$\sum_{k=1}^n \nu_k A_k = 0, \quad (3)$$

$$\sum_{k=1}^n \nu_k^* A_k = 0. \quad (4)$$

If for all $k = 1, 2, \dots, n$, $\nu_k^* = \lambda \nu_k$, $\lambda \neq 0$, then we say that the relations (3) and (4) are *stoichiometrically equivalent*.

In a number of recent works [2–7] a theory was elaborated, in which the sensitivity coefficients were expressed in terms of contributions associated with a class of stoichiometric relations between the species A_1, A_2, \dots, A_n . These relations were named *Hessian response equilibria* or, in short, *Hessian equilibria* (HEQs); their definition is given in the next section. In particular, it was demonstrated that [3]

$$\partial n_k / \partial Y = \delta + \frac{1}{\Delta} \sum_{[i]} \sum_{[j]} \mathbf{R} \begin{pmatrix} [i] \\ [j] \end{pmatrix} D([i], X) D([j], k) \quad (5)$$

and

$$\Delta = \frac{1}{m} \sum_{[i]} \sum_{[j]} \mathbf{R} \begin{pmatrix} [i] \\ [j] \end{pmatrix} L([i], [j]), \quad (6)$$

where $[i]$ and $[j]$ correspond to HEQs (see below) and the double summations embrace all pairs of HEQs. The meaning of the other symbols in eqs. (5) and (6) is specified later (in section 5). Equations (5) and (6) make it evident that the Hessian-response-equilibrium concept plays a decisive role in sensitivity analysis [2–7].

2. Definition of Hessian response equilibria

Although the HEQ-concept has its origin in (chemical) thermodynamics, the

definition of HEQs is based solely on the stoichiometric matrix, eq. (2). Thus, HEQs are stoichiometric and not thermodynamic notions.

In order to define the HEQs consider the determinant

$$D(i_1, i_2, \dots, i_{m-1}, k) = \begin{vmatrix} \nu_{1,i_1} & \nu_{1,i_2} & \dots & \nu_{1,i_{m-1}} & \nu_{1,k} \\ \nu_{2,i_1} & \nu_{2,i_2} & \dots & \nu_{2,i_{m-1}} & \nu_{2,k} \\ \dots & \dots & \dots & \dots & \dots \\ \nu_{m,i_1} & \nu_{m,i_2} & \dots & \nu_{m,i_{m-1}} & \nu_{m,k} \end{vmatrix}, \quad (7)$$

which is of order m , and which consists of the (i_1) th, (i_2) th, \dots , (i_{m-1}) th and k th columns of the stoichiometric matrix ν . In what follows the $(m-1)$ -tuple $(i_1, i_2, \dots, i_{m-1})$ will be abbreviated by $[i]$. Consequently, instead of $D(i_1, i_2, \dots, i_{m-1}, k)$ we sometimes write $D([i], k)$, as is the case in eq. (5). The $(m-1)$ -tuple $[i]$ is required to satisfy the conditions

$$1 \leq i_1 < i_2 < \dots < i_{m-1} \leq n. \quad (8)$$

In sensitivity analysis one encounters [2–7] certain stoichiometric relations of the form

$$\nu_1 A_1 + \nu_2 A_2 + \dots + \nu_n A_n = 0, \quad (9)$$

where

$$\nu_k = D([i], k), \quad k = 1, 2, \dots, n. \quad (10)$$

Equations (7)–(10) define a Hessian response equilibrium (HEQ)². It is seen that each HEQ is determined by a particular $(n-1)$ -tuple $[i]$. In view of this, the respective Hessian equilibrium will be denoted by $\mathcal{H}([i])$. In the next section (in lemma 1) we demonstrate that HEQs are linear combinations of SIRs. This, in particular, implies that relation (9), with the coefficients ν_k given via eq. (10), is stoichiometrically correct.

The following properties of HEQs are straightforward consequences of the above definition [2].

(a) The stoichiometric coefficient ν_k in eq. (9) is equal to zero whenever $k = i_1$ or $k = i_2$ or \dots $k = i_{m-1}$, because then two columns in the determinant (7) are equal. This means that the species $A_{i_1}, A_{i_2}, \dots, A_{i_{m-1}}$ have zero stoichiometric coefficients and are thus not involved in the Hessian equilibrium $\mathcal{H}([i])$.

(b) There are $\binom{n}{m-1}$ distinct choices of the species $A_{i_1}, A_{i_2}, \dots, A_{i_{m-1}}$ whose absence defines a particular HEQ. Therefore the number of HEQs is equal to $\binom{n}{m-1}$. Note that n is necessarily greater than m , and that $\binom{n}{m-1}$ is usually much greater than m . Throughout this paper it is assumed that $m > 1$.

(c) Not all HEQs need to be distinct: It often occurs that two different $(m-1)$ -

² Note that instead of ‘‘Hessian equilibrium’’ we earlier [2,3,5] used the term ‘‘Hessian reaction’’. This caused misunderstandings and was therefore abandoned.

tuples $[i]$ and $[j]$ pertain to stoichiometrically equivalent HEQs $\mathcal{H}([i])$ and $\mathcal{H}([j])$. It may happen that in some HEQs all stoichiometric coefficients are equal to zero.

3. The number of independent Hessian response equilibria is equal to m

In situations which are usually encountered in chemical thermodynamics, the parameters n and m have such values that the HEQs far outnumber the SIRs. We now demonstrate that, nevertheless, the chemical information contained in the HEQs and in the SIRs is precisely the same

THEOREM 1

The number of stoichiometrically independent Hessian response equilibria is equal to the number m of stoichiometrically independent reactions, specified via eqs. (1).

Proof

Theorem 1 is an immediate consequence of the below formulated lemmas 1 and 2. \square

LEMMA 1

Denote the number of independent HEQs by M . Then $M \leq m$.

Proof

The number of SIRs is m and they are independent by definition. The inequality stated in lemma 1 will be verified if we demonstrate that the HEQs are linear combinations of SIRs.

Denote by D_{jm} the minor obtained by deleting the j th row and the m th column from the determinant $D([i], k)$, eq. (7). Then,

$$\sum_{j=1}^m (-1)^{j+m} D_{jm} \nu_{jk} = D([i], k). \quad (11)$$

Multiply the j th SIR by $(-1)^{j+m} D_{jm}$ and sum over all $j = 1, 2, \dots, m$. Then by taking into account the identity (11),

$$\begin{aligned} \sum_{j=1}^m (-1)^{j+m} D_{jm} \left[\sum_{k=1}^n \nu_{jk} A_k \right] &= \sum_{k=1}^n \left[\sum_{j=1}^m (-1)^{j+m} D_{jm} \nu_{jk} \right] A_k \\ &= \sum_{k=1}^n D([i], k) A_k. \end{aligned} \quad (12)$$

The expression on the right-hand side of eq. (12) is just $\mathcal{H}([i])$. \square

LEMMA 2

With the same notation as in lemma 1, $M \geq m$.

Proof

The m SIRs in eqs. (1), are independent by definition. This is tantamount to the requirement that the rank of the stoichiometric matrix, eq. (2), is equal to m . The condition rank $\nu = m$ will hold if one can find $i_1, i_2, \dots, i_{m-1}, i_m$, such that the determinant

$$D(i_1, i_2, \dots, i_{m-1}, i_m) = \begin{vmatrix} \nu_{1,i_1} & \nu_{1,i_2} & \dots & \nu_{1,i_{m-1}} & \nu_{1,i_m} \\ \nu_{2,i_1} & \nu_{2,i_2} & \dots & \nu_{2,i_{m-1}} & \nu_{2,i_m} \\ \dots & \dots & \dots & \dots & \dots \\ \nu_{m,i_1} & \nu_{m,i_2} & \dots & \nu_{m,i_{m-1}} & \nu_{m,i_m} \end{vmatrix} \quad (13)$$

is different from zero. Without loss of generality we can label the species A_1, A_2, \dots, A_n so that $i_k = k$ for $k = 1, 2, \dots, m$. Then $D(1, 2, \dots, m - 1, m) = d$ is non-zero.

Order the HEQs so that the first HEQ is $\mathcal{H}(2, 3, 4, \dots, m - 1, m)$, the second HEQ is $\mathcal{H}(1, 3, 4, \dots, m - 1, m)$, the third HEQ is $\mathcal{H}(1, 2, 4, \dots, m - 1, m)$, ..., the $(m - 1)$ th HEQ is $\mathcal{H}(1, 2, 3, \dots, m - 2, m)$ and the m th HEQ is $\mathcal{H}(1, 2, 3, \dots, m - 2, m - 1)$. The remaining $\binom{n}{m-1} - m$ HEQs are ordered arbitrarily.

In accordance with eqs. (7), (9) and (10), the first m stoichiometric coefficients in the first HEQ are

$$\nu_1 = D(2, 3, 4, \dots, m - 1, m, 1),$$

$$\nu_2 = D(2, 3, 4, \dots, m - 1, m, 2),$$

$$\nu_3 = D(2, 3, 4, \dots, m - 1, m, 3),$$

...

$$\nu_{m-1} = D(2, 3, 4, \dots, m - 1, m, m - 1)$$

and

$$\nu_m = D(2, 3, 4, \dots, m - 1, m, m),$$

respectively. Bearing in mind eq. (13) we see that for the first HEQ

$$\nu_1 = (-1)^{m-1}d, \quad \nu_2 = \nu_3 = \nu_4 = \dots = \nu_{m-1} = \nu_m = 0.$$

In a fully analogous manner, for the second HEQ

$$\nu_2 = (-1)^{m-2}d, \quad \nu_1 = \nu_3 = \nu_4 = \dots = \nu_{m-1} = \nu_m = 0,$$

for the third HEQ

$$\nu_3 = (-1)^{m-3}d, \quad \nu_1 = \nu_2 = \nu_4 = \dots = \nu_{m-1} = \nu_m = 0,$$

etc., and for the m th HEQ

$$\nu_m = d, \quad \nu_1 = \nu_2 = \nu_3 = \dots = \nu_{m-2} = \nu_{m-1} = 0.$$

Thus, the stoichiometric matrix ν_H of the HEQs has the form

$$\nu_H = \begin{pmatrix} \pm d & 0 & 0 & 0 & \dots & 0 & 0 & \dots \\ 0 & \mp d & 0 & 0 & \dots & 0 & 0 & \dots \\ 0 & 0 & \pm d & 0 & \dots & 0 & 0 & \dots \\ \dots & & \dots & \dots & \dots & \dots & \dots & \dots \\ 0 & 0 & 0 & 0 & \dots & -d & 0 & \dots \\ 0 & 0 & 0 & 0 & \dots & 0 & d & \dots \\ \vdots & \vdots & \vdots & \vdots & & \vdots & \vdots & \end{pmatrix}. \tag{14}$$

From (14) is evident that the matrix ν_H possesses a square submatrix of order m , namely,

$$\begin{pmatrix} \pm d & 0 & 0 & 0 & \dots & 0 & 0 \\ 0 & \mp d & 0 & 0 & \dots & 0 & 0 \\ 0 & 0 & \pm d & 0 & \dots & 0 & 0 \\ \dots & & \dots & \dots & \dots & \dots & \dots \\ 0 & 0 & 0 & 0 & \dots & -d & 0 \\ 0 & 0 & 0 & 0 & \dots & 0 & d \end{pmatrix},$$

the determinant of which is equal to $\pm d^m$, and is thus non-zero. Therefore the rank of ν_H is at least m . □

4. The Hessian response equilibria are independent of the choice of the SIR-basis

As already mentioned, instead of the SIRs given by eqs. (1) we can use any of their linear combinations, say

$$\left. \begin{aligned} \nu'_{11}A_1 + \nu'_{12}A_2 + \dots + \nu'_{1n}A_n &= 0 \\ \nu'_{21}A_1 + \nu'_{22}A_2 + \dots + \nu'_{2n}A_n &= 0 \\ \dots & \dots \dots \\ \nu'_{m1}A_1 + \nu'_{m2}A_2 + \dots + \nu'_{mn}A_n &= 0 \end{aligned} \right\} \tag{15}$$

provided that the rank of the new stoichiometric matrix ν' ,

$$\mathbf{v}' = \begin{pmatrix} \nu'_{11} & \nu'_{12} & \dots & \nu'_{1n} \\ \nu'_{21} & \nu'_{22} & \dots & \nu'_{2n} \\ \dots & \dots & \dots & \dots \\ \nu'_{m1} & \nu'_{m2} & \dots & \nu'_{mn} \end{pmatrix}, \quad (16)$$

is also equal to m . Suppose that eqs. (1) are transformed into eqs. (15) in the following manner:

$$\sum_{k=1}^n \nu'_{hk} A_k = \sum_{j=1}^n T_{hj} \left[\sum_{i=1}^n \nu_{ji} A_i \right]. \quad (17)$$

Then the stoichiometric matrices \mathbf{v} and \mathbf{v}' , eqs. (2) and (16), are related via

$$\mathbf{v}' = \mathbf{T}\mathbf{v}, \quad (18)$$

where $\mathbf{T} = (T_{hk})$ is a square matrix of order m . In order to have $\text{rank } \mathbf{v} = \text{rank } \mathbf{v}'$, the determinant $|\mathbf{T}|$ of \mathbf{T} must differ from zero.

If $|\mathbf{T}| \neq 0$, then we say that eqs. (17) or (18) represent a transformation of the SIR-basis (1) into a new basis (15).

THEOREM 2

Let \mathcal{H} and \mathcal{H}' be two HEQs, pertaining to the same $(m - 1)$ -tuple $[i]$, but obtained from two different SIR-basis. Then \mathcal{H} and \mathcal{H}' are stoichiometrically equivalent.

Theorem 2 implies that the HEQs obtained from different SIRs differ only by a multiplicative constant (which, as will be shown in a while, is just the determinant of the transformation matrix \mathbf{T}). In other words, the form of the Hessian response equilibria is (up to a chemically insignificant multiplier) independent of the actual choice of the SIRs.

Proof

The Hessian reaction $\mathcal{H}'([i])$ corresponding to the SIRs (15) is

$$\nu'_1 A_1 + \nu'_2 A_2 + \dots + \nu'_n A_n = 0$$

with

$$\nu'_k = \begin{vmatrix} \nu'_{1,i_1} & \nu'_{1,i_2} & \dots & \nu'_{1,i_{m-1}} & \nu'_{1,k} \\ \nu'_{2,i_1} & \nu'_{2,i_2} & \dots & \nu'_{2,i_{m-1}} & \nu'_{2,k} \\ \dots & \dots & \dots & \dots & \dots \\ \nu'_{m,i_1} & \nu'_{m,i_2} & \dots & \nu'_{m,i_{m-1}} & \nu'_{m,k} \end{vmatrix}.$$

Now, because $\nu'_{ji} = (\mathbf{T}\mathbf{v})_{ji}$, $j = 1, 2, \dots, m$, $i = 1, 2, \dots, n$ (see eq. (18)), we have

$$\begin{aligned}
\nu'_k &= \begin{vmatrix} (\mathbf{T}\nu)_{1,i_1} & (\mathbf{T}\nu)_{1,i_2} & \dots & (\mathbf{T}\nu)_{1,i_{m-1}} & (\mathbf{T}\nu)_{1,k} \\ (\mathbf{T}\nu)_{2,i_1} & (\mathbf{T}\nu)_{2,i_2} & \dots & (\mathbf{T}\nu)_{2,i_{m-1}} & (\mathbf{T}\nu)_{2,k} \\ \dots & \dots & \dots & \dots & \dots \\ (\mathbf{T}\nu)_{m,i_1} & (\mathbf{T}\nu)_{m,i_2} & \dots & (\mathbf{T}\nu)_{m,i_{m-1}} & (\mathbf{T}\nu)_{m,k} \end{vmatrix} \\
&= \mathbf{T} \begin{vmatrix} \nu_{1,i_1} & \nu_{1,i_2} & \dots & \nu_{1,i_{m-1}} & \nu_{1,k} \\ \nu_{2,i_1} & \nu_{2,i_2} & \dots & \nu_{2,i_{m-1}} & \nu_{2,k} \\ \dots & \dots & \dots & \dots & \dots \\ \nu_{m,i_1} & \nu_{m,i_2} & \dots & \nu_{m,i_{m-1}} & \nu_{m,k} \end{vmatrix} \\
&= |\mathbf{T}| \begin{vmatrix} \nu_{1,i_1} & \nu_{1,i_2} & \dots & \nu_{1,i_{m-1}} & \nu_{1,k} \\ \nu_{2,i_1} & \nu_{2,i_2} & \dots & \nu_{2,i_{m-1}} & \nu_{2,k} \\ \dots & \dots & \dots & \dots & \dots \\ \nu_{m,i_1} & \nu_{m,i_2} & \dots & \nu_{m,i_{m-1}} & \nu_{m,k} \end{vmatrix} \\
&= |\mathbf{T}| \nu_k, \tag{19}
\end{aligned}$$

where ν_k is the respective stoichiometric coefficient of $\mathcal{H}([i])$, see eqs. (7), (9) and (10). Thus we showed that $\nu'_k = \lambda \nu_k$, for all $k = 1, 2, \dots, n$, where $\lambda = |\mathbf{T}| \neq 0$. Therefore, in accordance with eqs. (3) and (4), $\mathcal{H}'([i])$ and $\mathcal{H}([i])$ are stoichiometrically equivalent. \square

In view of eq. (10), a different way of writing eq. (19) is

$$D'([i], k) = |\mathbf{T}| D([i], k). \tag{20}$$

5. Discussion

By means of theorem 2 it is easy to show that the right-hand side of eq. (5) is independent of the choice of the SIR-basis.

The symbols used in eqs. (5) and (6) have the following meanings [4]:

$\delta = 1$ if Y is the initial amount of the species A_k , and $\delta = 0$ otherwise;

$$\mathbf{R} \begin{pmatrix} [j] \\ [j] \end{pmatrix} = \begin{vmatrix} R_{i_1 j_1} & R_{i_1 j_2} & \dots & R_{i_1 j_{m-1}} \\ R_{i_2 j_1} & R_{i_2 j_2} & \dots & R_{i_2 j_{m-1}} \\ \dots & \dots & \dots & \dots \\ R_{i_{m-1} j_1} & R_{i_{m-1} j_2} & \dots & R_{i_{m-1} j_{m-1}} \end{vmatrix}, \tag{21}$$

where

$$R_{rs} = \frac{1}{RT} \left(\frac{\partial^2 G}{\partial n_r \partial n_s} \right), \tag{22}$$

with G denoting the Gibbs energy of the system examined, while n_r and n_s stand for equilibrium amounts of the species A_r and A_s ;

$$D([i], X) = \begin{vmatrix} \nu_{1,i_1} & \nu_{1,i_2} & \dots & \nu_{1,i_{m-1}} & X_1 \\ \nu_{2,i_1} & \nu_{2,i_2} & \dots & \nu_{2,i_{m-1}} & X_2 \\ \dots & \dots & \dots & \dots & \dots \\ \nu_{m,i_1} & \nu_{m,i_2} & \dots & \nu_{m,i_{m-1}} & X_m \end{vmatrix}, \tag{23}$$

where X_j is a parameter associated with the j th SIR (for details see [2–5]);

$$L([i], [j]) = \sum_{r=1}^n \sum_{s=1}^n D([i], r) D([j], s) R_{rs}. \tag{24}$$

The determinants $D([i], k)$ in eq. (5) as well as $D([i], r)$ and $D([j], s)$ in the expression (24) were previously defined via eq. (7).

The quantity Δ , eq. (6) is called the Hessian determinant [2].

The matrix element R_{rs} is defined in terms of G , n_r and n_s (see eq. (22)), for which the choice of SIRs is immaterial. Consequently, $\mathbf{R} \begin{pmatrix} [i] \\ [j] \end{pmatrix}$, eq. (21), is also independent of the SIR-basis.

Let $L'([i], [j])$ be the quantity analogous to $L([i], [j])$, but calculated using the SIR-basis (15). Then, in view of eqs. (10) and (20),

$$\begin{aligned} L'([i], [j]) &= \sum_{r=1}^n \sum_{s=1}^n D'([i], r) D'([j], s) R_{rs} \\ &= \sum_{r=1}^n \sum_{s=1}^n [|\mathbf{T}| D([i], r)] [|\mathbf{T}| D([j], s)] R_{rs} = |\mathbf{T}|^2 L([i], [j]). \end{aligned}$$

From eq. (6) it now immediately follows that

$$\Delta' = |\mathbf{T}|^2 \Delta. \tag{25}$$

The reaction parameter X'_h , associated with the h th SIR from the basis (15), is obtained from the SIR-basis (1) according to [2]

$$X'_h = \sum_{j=1}^n T_{hj} X_j,$$

where the multipliers T_{hj} are the same as those occurring in eq. (17). This implies

$$\begin{pmatrix} X'_1 \\ X'_2 \\ \vdots \\ X'_m \end{pmatrix} = \mathbf{T} \begin{pmatrix} X_1 \\ X_2 \\ \vdots \\ X_m \end{pmatrix}$$

and in a way fully analogous to the proof of theorem 2 we obtain from eq. (23)

$$D'([i], X) = |\mathbf{T}| D([i], X). \quad (26)$$

Bearing in mind eqs. (20), (25) and (26), as well as the SIR-independence of $\mathbf{R} \begin{pmatrix} [i] \\ [j] \end{pmatrix}$, we can now directly check that the right-hand side of eq. (5) has the same value for all choices of the SIR-basis.

However, by the same argument we see something more: Each summand occurring on the right-hand side of eq. (5), namely,

$$\psi([i], [j]) = \frac{1}{\Delta} \mathbf{R} \begin{pmatrix} [i] \\ [j] \end{pmatrix} D([i], X) D([j], k),$$

is independent of the SIR-basis. As discussed in detail elsewhere [4], the quantity $\psi([i], [i])$ represents the contribution of the Hessian response equilibrium $\mathcal{H}([i])$ to the sensitivity coefficient $\partial n_k / \partial Y$; if $[i] \neq [j]$, then $\psi([i], [j])$ is the respective contribution of a pair of HEQs, $\mathcal{H}([i])$ and $\mathcal{H}([j])$. Thus, the invariance to the choice of the SIRs applies not only to the sensitivity coefficients (which is a well known result), but also to the decomposition of sensitivity coefficients into contributions coming from HEQs and pairs of HEQs. This latter finding may be considered as a further support for the plausibility of using Hessian response equilibria in sensitivity analysis.

Using theorem 2, we could deduce lemma 2 in an alternative way. Since the HEQ-basis is same for all choices of SIRs, we first transform the initial SIRs, eqs. (1), into a linear combination in which the stoichiometric matrix has the form

$$\mathbf{v}'' = \begin{pmatrix} 1 & 0 & 0 & \cdots & 0 & \nu''_{1,m+1} & \nu''_{1,m+2} & \cdots & \nu''_{1,n} \\ 0 & 1 & 0 & \cdots & 0 & \nu''_{2,m+1} & \nu''_{2,m+2} & \cdots & \nu''_{2,n} \\ \cdots & & & \cdots & & \cdots & \cdots & \cdots & \cdots \\ 0 & 0 & 0 & \cdots & 1 & \nu''_{m,m+1} & \nu''_{m,m+2} & \cdots & \nu''_{m,n} \end{pmatrix}.$$

The rank-preserving transformation $\mathbf{v} \rightarrow \mathbf{v}''$ is achieved by standard methods of linear algebra. It is now straightforward to recognize that each row of the matrix \mathbf{v}'' corresponds to an HEQ. These HEQs are necessarily independent.

In this paper we established some fundamental features of the Hessian response equilibrium concept. By this we hope that its future use in chemical thermodynamics (and elsewhere?) will be easier and with greater confidence. This results communicated here demonstrate that HEQs are mathematically well-defined

objects, possessing remarkable properties, and deserving the attention of mathematicians and mathematical chemists.

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