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An identity in chemical thermodynamics

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In this work we consider the equilibrium state of a multicomponent system in which chemical reactions occur, and its sensitivity to the change of any of the thermodynamic parameters influencing the equilibrium. A general expression is obtained for the sensitivity coefficient $\partial n_i/\partial Y$, where n_i is the equilibrium amount of the ith chemical species in the system, and Y is a thermodynamic parameter such as temperature, pressure, initial amount of a species, chemical potential of a species, etc. We demonstrate that the sensitivity coefficients are linear combinations of contributions originating from certain special reactions, called response reactions, which are defined in the paper.

1. Introduction

A general problem of chemical thermodynamics is to describe the response of the equilibrium state of a multicomponent system in which chemical reactions occur, to the change of one (or more) parameters that influence the equilibrium [1]. A particular aspect of this problem is the dependence of the equilibrium composition of such a system on various thermodynamic parameters [2,3]. This dependence if measured by the so-called sensitivity coefficients $\partial n_i/\partial Y$, where n_i is the equilibrium amount of the ith chemical species in the system considered, and Y is the respective parameter. In this paper we deduce a general expression for the sensitivity coefficients. It seems that this result was hitherto not known in chemical thermodynamics.

In the system considered in this work we assume that chemical reactions occur between n distinct species A_1, A_2, ..., A_n. The interactions between them are described by means of m chemical equations:

$$\nu_{j1}A_1 + \nu_{j2}A_2 + \ldots + \nu_{jn}A_n = 0\,, \quad j = 1,2,\ldots,m\,. \tag{1}$$

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The stoichiometric coefficients ν_{ji} are chosen so that $\nu_{ji}<0$ if A_i is a reactant, $\nu_{ji}>0$ if A_i is a product, and $\nu_{ji}=0$ if A_i does not participate in the jth reaction. Throughout this paper it is assumed that eqs. (1) are stoichiometrically independent, i.e. that

$$\operatorname{rank}\left\| \begin{matrix} \nu_{11} & \nu_{12} & \dots & \nu_{1n} \\ \nu_{21} & \nu_{22} & \dots & \nu_{2n} \\ \dots & & \dots & \\ \nu_{m1} & \nu_{m2} & \dots & \nu_{mn} \end{matrix} \right\| = m$$

and that $m>1$. Recall that the chemical reactions (1) can be chosen in many different, but (from the point of view of the thermodynamics of multiple chemical equilibria) equivalent ways.

We further assume ideal behavior of the system. The concrete realization of this assumption is eq. (4), see below, which is supposed to be always satisfied.

The sum of the of the stoichiometric coefficients of the jth reaction (1), namely $\nu_{j1}+\nu_{j2}+\ldots+\nu_{jn}$, will be denoted by $\Delta\nu_j$.

By n_{i0} and n_i we denote the initial and equilibrium amounts (= numbers of moles), respectively, of the ith chemical species A_i. The total amount of substances present in the system at equilibrium is n_t. If n_z is the amount of the "inert" substances, i.e., those which do not participate in any of the chemical processes (1), then

$$n_t = n_z + \sum_{i=1}^{n} n_i \,.$$

The extent of the jth reaction (1) at equilibrium will be denoted by ξ_j, $j=1, 2, \ldots, m$. Then the mass-balance conditions read

$$n_i = n_{i0} + \sum_{j=1}^{m} \nu_{ji}\xi_j \,, \quad i=1,2,\ldots,n \,. \tag{2}$$

Let Y be the parameter whose influence on the equilibrium composition will be examined. Then the respective sensitivity coefficients are $\partial n_i/\partial Y$, $i=1,2,\ldots,n$, and they satisfy the equations

$$\partial n_i/\partial Y = \delta + \sum_{j=1}^{m} \nu_{ji}\partial\xi_j/\partial Y \,, \quad i=1,2,\ldots,n \,, \tag{3}$$

where $\delta=1$ if $Y=n_{i0}$ and $\delta=0$ otherwise. Equations (3) are immediate consequences of (2).

The Gibbs energy of the system considered, G, can be viewed as a function of the parameters ξ_1, ξ_2, …, ξ_m. In view of this, we may define the quantities G_{rs} [1,2],

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

If we accept that the behavior of our system is ideal, then the following identity is known to be obeyed [1,2]:

$$G_{rs} = \sum_{i=1}^{n} \frac{\nu_{ri} \nu_{si}}{n_i} - \frac{1}{n_t} \Delta\nu_r \Delta\nu_s . \tag{4}$$

These second derivatives of the Gibbs energy play a central role in the study of the sensitivity coefficients, because of the relations [2]

$$G_{j1} \, \partial\xi_1/\partial Y + G_{j2} \, \partial\xi_2/\partial Y + \ldots + G_{jm} \, \partial\xi_m/\partial Y = X_j, \quad j = 1, 2, \ldots, m . \tag{5}$$

The quantity X_j, which appears on the right-hand side of (5), is associated with the jth chemical reaction (1), $j = 1, 2, \ldots, m$. Besides, X_j depends on the nature of the parameter Y. In table 1 are listed some usual choices for Y and the corresponding expressions for X_j.

Observing that (5) is a system of m linear equations in the unknowns $\partial\xi_j/\partial Y$, $j = 1, 2, \ldots, m$, we immediately conclude that

$$\partial\xi_j/\partial Y = \Delta_j/\Delta , \tag{6}$$

where Δ and Δ_j are determinants, given by

$$\Delta = \begin{vmatrix} G_{11} & G_{12} & \ldots & G_{1m} \\ G_{21} & G_{22} & \ldots & G_{2m} \\ \ldots & \ldots & & \ldots \\ G_{m1} & G_{m2} & \ldots & G_{mm} \end{vmatrix}$$

and

Table 1
The form of the function X_j (eq. (5)) for various choices of the parameter Y, in the case of systems with ideal behavior.

Y	X_j
T	$\frac{\Delta H_j^0}{RT^2}$
$\ln P$	$-\Delta\nu_j$
n_z	$\frac{\Delta\nu_j}{n_t}$
n_{k0}	$-\left[\frac{\nu_{kj}}{n_k} - \frac{\Delta\nu_j}{n_t}\right]$
μ_k^0	$-\frac{\nu_{kj}}{RT}$

$$\Delta_j = \begin{vmatrix} G_{11} & G_{12} & \dots & G_{1,j-1} & X_1 & G_{1,j+1} & \dots & G_{1m} \\ G_{21} & G_{22} & \dots & G_{2,j-1} & X_2 & G_{2,j+1} & \dots & G_{2m} \\ \dots & \dots & & \dots & \dots & \dots & & \dots \\ G_{m1} & G_{m2} & \dots & G_{m,j-1} & X_m & G_{m,j+1} & \dots & G_{mm} \end{vmatrix} . \qquad (7)$$

Substituting (6) back into (3) we arrive at

$$\partial n_i/\partial Y = \delta + \frac{1}{\Delta}\sum_{j=1}^{m} \nu_{ji}\Delta_j \, . \qquad (8)$$

Formula (8) is the starting point for the present considerations.

2. The identity: first formulation

To be able to formulate an expression for the sensitivity coefficients, we introduce the following abbreviations for the four types of determinants that occur in our considerations:

$$D(i_1, i_2, \dots, i_{m-1}, i) = \begin{vmatrix} \nu_{1,i_1} & \nu_{1,i_2} & \dots & \nu_{1,i_{m-1}} & \nu_{1,i} \\ \nu_{2,i_1} & \nu_{2,i_2} & \dots & \nu_{2,i_{m-1}} & \nu_{2,i} \\ \vdots & \vdots & & \vdots & \vdots \\ \nu_{m,i_1} & \nu_{m,i_2} & \dots & \nu_{m,i_{m-1}} & \nu_{m,i} \end{vmatrix} , \qquad (9)$$

$$D(i_1, i_2, \dots, i_{m-1}, X) = \begin{vmatrix} \nu_{1,i_1} & \nu_{1,i_2} & \dots & \nu_{1,i_{m-1}} & X_1 \\ \nu_{2,i_1} & \nu_{2,i_2} & \dots & \nu_{2,i_{m-1}} & X_2 \\ \vdots & \vdots & & \vdots & \vdots \\ \nu_{m,i_1} & \nu_{m,i_2} & \dots & \nu_{m,i_{m-1}} & X_m \end{vmatrix} , \qquad (10)$$

$$D(i_1, i_2, \dots, i_{m-2}, \Delta\nu, i) = \begin{vmatrix} \nu_{1,i_1} & \nu_{1,i_2} & \dots & \nu_{1,i_{m-2}} & \Delta\nu_1 & \nu_{1,i} \\ \nu_{2,i_1} & \nu_{2,i_2} & \dots & \nu_{2,i_{m-2}} & \Delta\nu_2 & \nu_{2,i} \\ \vdots & \vdots & & \vdots & \vdots & \vdots \\ \nu_{m,i_1} & \nu_{m,i_2} & \dots & \nu_{m,i_{m-2}} & \Delta\nu_m & \nu_{m,i} \end{vmatrix} , \qquad (11)$$

$$D(i_1, i_2, \dots, i_{m-2}, \Delta\nu, X) = \begin{vmatrix} \nu_{1,i_1} & \nu_{1,i_2} & \dots & \nu_{1,i_{m-2}} & \Delta\nu_1 & X_1 \\ \nu_{2,i_1} & \nu_{2,i_2} & \dots & \nu_{2,i_{m-2}} & \Delta\nu_2 & X_2 \\ \vdots & \vdots & & \vdots & \vdots & \vdots \\ \nu_{m,i_1} & \nu_{m,i_2} & \dots & \nu_{m,i_{m-2}} & \Delta\nu_m & X_m \end{vmatrix} . \qquad (12)$$

Then the following identity holds:

$$\partial n_i/\partial Y = \delta + \frac{1}{\Delta}\left[\sum_{i_1<i_2<\ldots<i_{m-1}} \frac{D(i_1,i_2,\ldots,i_{m-1},i)D(i_1,i_2,\ldots,i_{m-1},X)}{n_{i_1}n_{i_2}\ldots n_{i_{m-1}}} \right.$$
$$\left. + \frac{1}{n_t} \sum_{i_1<i_2<\ldots<i_{m-2}} \frac{D(i_1,i_2,\ldots,i_{m-2},\Delta\nu,i)D(i_1,i_2,\ldots,i_{m-2},\Delta\nu,X)}{n_{i_1}n_{i_2}\ldots n_{i_{m-2}}} \right]. \tag{13}$$

In order to be able to see the chemical meaning of the above formula we introduce an auxiliary notion, namely the response reactions. We further classify the response reactions into Hessian (HR) and non-Hessian (NHR).

3. Two special types of stoichiometric relations: Hessian and non-Hessian response reactions

Any linear combination of the chemical equations (1) results in a new "chemical reaction" between the species A_1, A_2, …, A_n, which is acceptable from a stoichiometric point of view. In what follows we shall be interested in certain special types of such linear combinations, which we name "*response reactions*", because these reactions are intimately connected with the sensitivity coefficients. We distinguish between "*Hessian response reactions*" (which are connected with the determinant of the Hessian matrix of the Gibbs energy [4]) and "*non-Hessian response reactions*" (which have no effect on the Hessian determinant).

A linear combination of eqs. (1) is said to be a Hessian response reaction (HR), or shorter: a Hessian reaction, if it involves at most $n-m+1$ of the chemical species A_i, $i = 1,2,\ldots,n$. The HR in which the species A_{i_1}, A_{i_2}, …, $A_{i_{m-1}}$ are absent will be denoted by $\mathcal{H} = \mathcal{H}(i_1,i_2,\ldots,i_{m-1})$. If this reaction is written in the form

$$\sum_{i=1}^{n} \nu_i(\mathcal{H})A_i = 0$$

then it can be shown that its stoichiometric coefficients satisfy

$$\nu_i(\mathcal{H}) = D(i_1,i_2,\ldots,i_{m-1},i)\,. \tag{14}$$

Furthermore, the change of the quantity X in the reaction $\mathcal{H}(i_1,i_2,\ldots,i_{m-1})$ is equal to

$$X(\mathcal{H}) = D(i_1,i_2,\ldots,i_{m-1},X)\,. \tag{15}$$

More details on the HRs can be found elsewhere [4]. In particular, in [4] was shown that the Hessian determinant of a multicomponent equilibrium system is equal to the sum of contributions coming from the HRs.

A linear combination of eqs. (1) is said to be a non-Hessian response reaction (NHR), or shorter: a non-Hessian reaction, if it involves at most $n-m+2$ of the chemical species A_i, $i = 1, 2, \ldots, n$, and if the sum of its stoichiometric coefficients is equal to zero. The NHR in which the species A_{i_1}, A_{i_2}, ..., $A_{i_{m-2}}$ are absent will be denoted by $\mathcal{N} = \mathcal{N}(i_1, i_2, \ldots, i_{m-2})$. If this reaction is written in the form

$$\sum_{i=1}^{n} \nu_i(\mathcal{N}) A_i = 0$$

then in full analogy with (14) and (15),

$$\nu_i(\mathcal{N}) = D(i_1, i_2, \ldots, i_{m-2}, \Delta\nu, i)$$

and

$$X(\mathcal{N}) = D(i_1, i_2, \ldots, i_{m-2}, \Delta\nu, X) .$$

Notice that there may exist an overlap between the two above described sets of reactions: a NHR may simultaneously be a HR and vice versa. A detailed discussion on the concept of NHRs and their role in determining the properties of chemical equilibria, together with a number of applications to concrete physicochemical systems, will be given in a later publication [5].

4. The identity: second formulation

Using the concept introduced in the preceding section, we can rewrite the formula (13) as

$$\partial n_i/\partial Y = \delta + \frac{1}{\Delta}\left[\sum_{\mathcal{H}} \nu_i(\mathcal{H}) X(\mathcal{H}) \pi(\mathcal{H}) + \frac{1}{n_t}\sum_{\mathcal{N}} \nu_i(\mathcal{N}) X(\mathcal{N}) \pi(\mathcal{N})\right] , \tag{16}$$

where

$$\pi(\mathcal{H}) = \frac{1}{n_{i_1} n_{i_2} \ldots n_{i_{m-1}}} ; \quad \pi(\mathcal{N}) = \frac{1}{n_{i_1} n_{i_2} \ldots n_{i_{m-2}}} .$$

The first summation on the right-hand side of (16) embraces the Hessian reactions $\mathcal{H} = \mathcal{H}(i_1, i_2, \ldots, i_{m-1})$ whereas the second summations goes over the non-Hessian reactions $\mathcal{N} = \mathcal{N}(i_1, i_2, \ldots, i_{m-2})$. Consequently, every sensitivity coefficient can be viewed as being equal to the sum of contributions coming from all response reactions; the contributions coming from HRs have a different form than those associated with NHRs. This observation enables a deeper insight into the perplexed interrelations which determine the thermodynamic behavior of multicomponent systems with multiple chemical equilibria. Numerous applications of (16) will be elaborated elsewhere [5].

5. Proof of formula (13)

We divide the proof of formula (13) into three steps. In the first step we show that the sensitivity coefficients can be written in the form

$$\partial n_i/\partial Y = \delta + \frac{1}{\Delta}\left(\Lambda_1 + \frac{1}{n_t}\Lambda_2\right). \tag{17}$$

In the second and third steps we demonstrate that

$$\Lambda_1 = \sum_{i_1<i_2<\ldots<i_{m-1}} \frac{D(i_1,i_2,\ldots,i_{m-1},i)D(i_1,i_2,\ldots,i_{m-1},X)}{n_{i_1}n_{i_2}\ldots n_{i_{m-1}}} \tag{18}$$

and

$$\Lambda_2 = \sum_{i_1<i_2<\ldots<i_{m-2}} \frac{D(i_1,i_2,\ldots,i_{m-2},\Delta\nu,i)D(i_1,i_2,\ldots,i_{m-2},\Delta\nu,X)}{n_{i_1}n_{i_2}\ldots n_{i_{m-2}}}. \tag{19}$$

with the terms in the numerators being given via eqs. (9)–(12).

Step 1

In the first part of the proof of formula (13) we utilize the following two properties of determinants:

$$\begin{vmatrix} a_{11} & a_{12} & \ldots & a'_{1h}+a''_{1h} & \ldots & a_{1m} \\ a_{11} & a_{12} & \ldots & a'_{1h}+a''_{1h} & \ldots & a_{1m} \\ \ldots & \ldots & & \ldots\quad\ldots & & \ldots \\ a_{11} & a_{12} & \ldots & a'_{1h}+a''_{1h} & \ldots & a_{1m} \end{vmatrix} = \begin{vmatrix} a_{11} & a_{12} & \ldots & a'_{1h} & \ldots & a_{1m} \\ a_{11} & a_{12} & \ldots & a'_{1h} & \ldots & a_{1m} \\ \ldots & \ldots & & \ldots & & \ldots \\ a_{11} & a_{12} & \ldots & a'_{1h} & \ldots & a_{1m} \end{vmatrix}$$

$$+ \begin{vmatrix} a_{11} & a_{12} & \ldots & a''_{1h} & \ldots & a_{1m} \\ a_{11} & a_{12} & \ldots & a''_{1h} & \ldots & a_{1m} \\ \ldots & \ldots & & \ldots & & \ldots \\ a_{11} & a_{12} & \ldots & a''_{1h} & \ldots & a_{1m} \end{vmatrix} \tag{20}$$

and

$$\begin{vmatrix} a_{11} & a_{12} & \ldots & \lambda a_{1h} & \ldots & a_{1m} \\ a_{11} & a_{12} & \ldots & \lambda a_{1h} & \ldots & a_{1m} \\ \ldots & \ldots & & \ldots & & \ldots \\ a_{11} & a_{12} & \ldots & \lambda a_{1h} & \ldots & a_{1m} \end{vmatrix} = \lambda \begin{vmatrix} a_{11} & a_{12} & \ldots & a_{1h} & \ldots & a_{1m} \\ a_{11} & a_{12} & \ldots & a_{1h} & \ldots & a_{1m} \\ \ldots & \ldots & & \ldots & & \ldots \\ a_{11} & a_{12} & \ldots & a_{1h} & \ldots & a_{1m} \end{vmatrix}. \tag{21}$$

Introducing the abbreviation

$$G^*_{rs} = \sum_{i=1}^{n} \frac{\nu_{ri}\nu_{si}}{n_i} \tag{22}$$

we can rewrite eq. (4) in the form

$$G_{rs} = G^*_{rs} - \frac{1}{n_t}\Delta\nu_r\Delta\nu_s. \tag{23}$$

Then by substituting (23) back into (7), and by bearing in mind (20) and (21), (with $h = 1$), we obtain

$$\Delta_j = \begin{vmatrix} G^*_{11} & G_{12} & \dots & G_{1,j-1} & X_1 & G_{1,j+1} & \dots & G_{1m} \\ G^*_{21} & G_{22} & \dots & G_{2,j-1} & X_2 & G_{2,j+1} & \dots & G_{2m} \\ \dots & \dots & & \dots & \dots & \dots & & \dots \\ G^*_{m1} & G_{m2} & \dots & G_{m,j-1} & X_m & G_{m,j+1} & \dots & G_{mm} \end{vmatrix}$$

$$- \frac{\Delta\nu_1}{n_t} \begin{vmatrix} \Delta\nu_1 & G_{12} & \dots & G_{1,j-1} & X_1 & G_{1,j+1} & \dots & G_{1m} \\ \Delta\nu_2 & G_{22} & \dots & G_{2,j-1} & X_2 & G_{2,j+1} & \dots & G_{2m} \\ \dots & \dots & & \dots & \dots & \dots & & \dots \\ \Delta\nu_m & G_{m2} & \dots & G_{m,j-1} & X_m & G_{m,j+1} & \dots & G_{mm} \end{vmatrix} .$$

Repeating the same procedure for the second column ($h = 2$) we further get

$$\Delta_j = \begin{vmatrix} G^*_{11} & G^*_{12} & \dots & G_{1,j-1} & X_1 & G_{1,j+1} & \dots & G_{1m} \\ G^*_{21} & G^*_{22} & \dots & G_{2,j-1} & X_2 & G_{2,j+1} & \dots & G_{2m} \\ \dots & \dots & & \dots & \dots & \dots & & \dots \\ G^*_{m1} & G^*_{m2} & \dots & G_{m,j-1} & X_m & G_{m,j+1} & \dots & G_{mm} \end{vmatrix}$$

$$- \frac{\Delta\nu_2}{n_t} \begin{vmatrix} G^*_{12} & \Delta\nu_1 & \dots & G_{1,j-1} & X_1 & G_{1,j+1} & \dots & G_{1m} \\ G^*_{22} & \Delta\nu_2 & \dots & G_{2,j-1} & X_2 & G_{2,j+1} & \dots & G_{2m} \\ \dots & \dots & & \dots & \dots & \dots & & \dots \\ G^*_{m2} & \Delta\nu_m & \dots & G_{m,j-1} & X_m & G_{m,j+1} & \dots & G_{mm} \end{vmatrix}$$

$$- \frac{\Delta\nu_1}{n_t} \begin{vmatrix} \Delta\nu_1 & G^*_{12} & \dots & G_{1,j-1} & X_1 & G_{1,j+1} & \dots & G_{1m} \\ \Delta\nu_2 & G^*_{22} & \dots & G_{2,j-1} & X_2 & G_{2,j+1} & \dots & G_{2m} \\ \dots & \dots & & \dots & \dots & \dots & & \dots \\ \Delta\nu_m & G^*_{m2} & \dots & G_{m,j-1} & X_m & G_{m,j+1} & \dots & G_{mm} \end{vmatrix}$$

$$+ \left(- \frac{\Delta\nu_1}{n_t} \right) \left(- \frac{\Delta\nu_2}{n_t} \right) \begin{vmatrix} \Delta\nu_1 & \Delta\nu_1 & \dots & G_{1,j-1} & X_1 & G_{1,j+1} & \dots & G_{1m} \\ \Delta\nu_2 & \Delta\nu_2 & \dots & G_{2,j-1} & X_2 & G_{2,j+1} & \dots & G_{2m} \\ \dots & \dots & & \dots & \dots & \dots & & \dots \\ \Delta\nu_m & \Delta\nu_m & \dots & G_{m,j-1} & X_m & G_{m,j+1} & \dots & G_{mm} \end{vmatrix} .$$

The last determinant in the above expression is zero because two of its columns coincide.

Continuing the same reasoning for the remaining columns of Δ_j (except, of course, for the jth column), we finally arrive at

$$\Delta_j = \Delta^*_j - \frac{1}{n_t} \sum_{\substack{k=1 \\ (k \neq j)}} \Delta\nu_k \Delta^*_{j,k} , \tag{24}$$

where

$$\Delta_j^* = \begin{vmatrix} G_{11}^* & G_{12}^* & \dots & G_{1,j-1}^* & X_1 & G_{1,j+1}^* & \dots & G_{1m}^* \\ G_{21}^* & G_{22}^* & \dots & G_{2,j-1}^* & X_2 & G_{2,j+1}^* & \dots & G_{2m}^* \\ \dots & \dots & & \dots & \dots & \dots & & \dots \\ G_{m1}^* & G_{m2}^* & \dots & G_{m,j-1}^* & X_m & G_{m,j+1}^* & \dots & G_{mm}^* \end{vmatrix} \tag{25}$$

and

$$\Delta_{j,k}^* = \begin{vmatrix} G_{11}^* & G_{12}^* & \dots & G_{1,j-1}^* & X_1 & G_{1,j+1}^* & \dots & G_{1,k-1}^* & \Delta\nu_1 & G_{1,k+1}^* & \dots & G_{1m}^* \\ G_{21}^* & G_{22}^* & \dots & G_{2,j-1}^* & X_2 & G_{2,j+1}^* & \dots & G_{2,k-1}^* & \Delta\nu_2 & G_{2,k+1}^* & \dots & G_{2m}^* \\ \dots & \dots & & \dots & \dots & \dots & & \dots & \dots & \dots & & \dots \\ G_{m1}^* & G_{m2}^* & \dots & G_{m,j-1}^* & X_m & G_{m,j+1}^* & \dots & G_{m,k-1}^* & \Delta\nu_m & G_{m,k+1}^* & \dots & G_{mm}^* \end{vmatrix} . \tag{26}$$

Equation (8) can now be written in the form (17) provided

$$\Lambda_1 = \sum_{j=1}^{m} \nu_{ji} \Delta_j^* \tag{27}$$

and

$$\Lambda_2 = -\sum_{j=1}^{m} \nu_{ji} \sum_{\substack{k=1 \\ (k \neq j)}}^{m} \Delta\nu_k \Delta_{j,k}^* . \tag{28}$$

Step 2

We now proceed to show that (18) follows from (27). In order to do this we first expand Δ_j^*, eq. (25), with respect to its jth column. Then

$$\Lambda_1 = \sum_{j=1}^{m} \nu_{ji} \sum_{k=1}^{m} (-1)^{k+j} X_k \Delta^*(k|j) . \tag{29}$$

Here Δ^* stands for the determinant

$$\Delta^* = \begin{vmatrix} G_{11}^* & G_{12}^* & \dots & G_{1m}^* \\ G_{21}^* & G_{22}^* & \dots & G_{2m}^* \\ \dots & \dots & & \dots \\ G_{m1}^* & G_{m2}^* & \dots & G_{mm}^* \end{vmatrix}$$

whereas $\Delta^*(kh\dots|jl\dots)$ is the minor, obtained from Δ^* by deleting its kth, hth, ... rows and jth, lth, ... columns.

Taking into account the form of the matrix elements G_{rs}^*, eq. (22), and using the properties (20) and (21), expand $\Delta^*(k|j)$ with respect to all its $m-1$ columns. This results in

$$\Delta^*(k|j) = \sum_{i_1=1}^{n}\sum_{i_2=1}^{n}\cdots\sum_{i_{m-1}=1}^{n} \frac{\nu_{1,i_1}\nu_{2,i_2}\ldots\nu_{j-1,i_{j-1}}\nu_{j+1,i_j}\ldots\nu_{m,i_{m-1}}}{n_{i_1}n_{i_2}\ldots n_{i_{m-1}}}$$

$$\times \begin{vmatrix} \nu_{1,i_1} & \nu_{1,i_2} & \ldots & \nu_{1,i_{m-1}} \\ \nu_{2,i_1} & \nu_{2,i_2} & \ldots & \nu_{2,i_{m-1}} \\ \ldots & \ldots & & \ldots \\ \nu_{k-1,i_1} & \nu_{k-1,i_2} & \ldots & \nu_{k-1,i_{m-1}} \\ \nu_{k+1,i_1} & \nu_{k+1,i_2} & \ldots & \nu_{k+1,i_{m-1}} \\ \ldots & \ldots & & \ldots \\ \nu_{m,i_1} & \nu_{m,i_2} & \ldots & \nu_{m,i_{m-1}} \end{vmatrix} . \qquad (30)$$

The determinant on the right-hand side of (30) is just a minor of the determinant ν,

$$\boldsymbol{\nu} = \boldsymbol{\nu}(i_1, i_2, \ldots, i_m) = \begin{vmatrix} \nu_{1,i_1} & \nu_{1,i_2} & \ldots & \nu_{1,i_{m-1}} & \nu_{1,i_m} \\ \nu_{2,i_1} & \nu_{2,i_2} & \ldots & \nu_{2,i_{m-1}} & \nu_{2,i_m} \\ \ldots & \ldots & & \ldots & \\ \nu_{m,i_1} & \nu_{m,i_2} & \ldots & \nu_{m,i_{m-1}} & \nu_{m,i_m} \end{vmatrix}$$

obtained from $\boldsymbol{\nu}$ by deleting its kth row and mth column. Therefore we denote this minor by $\boldsymbol{\nu}(k|m) = \boldsymbol{\nu}(i_1, i_2, \ldots, i_m)(k|m)$.

If any two of the indices i_1, i_2, …, i_{m-1} are mutually equal, then the respective columns in $\boldsymbol{\nu}(k|m)$ coincide, and, therefore, the corresponding summand in (30) becomes equal to zero. We thus have to examine only those summands on the right-hand side of (30), in which all the indices $i_1, i_2, \ldots, i_{m-1}$ are mutually distinct.

Let $(h_1, h_2, \ldots, h_{m-1})$ be an ordered m-tuple of integers, such that $1 \leqslant h_1 < h_2 < \ldots < h_{m-1} \leqslant n$. Then one of the summands in (30) will be of the form

$$\frac{\nu_{1,i_1}\nu_{2,i_2}\ldots\nu_{j-1,i_{j-1}}\nu_{j+1,i_j}\ldots\nu_{m,i_{m-1}}}{n_{i_1}n_{i_2}\ldots n_{i_{m-1}}} \cdot \boldsymbol{\nu}(h_1, h_2, \ldots, h_{m-1}, h_m)(k|m) . \qquad (31)$$

Note that h_m in $\boldsymbol{\nu}(h_1, h_2, \ldots, h_{m-1}, h_m)(k|m)$ is a dummy parameter, because in $\boldsymbol{\nu}(h_1, h_2, \ldots, h_{m-1}, h_m)(k|m)$, the mth column of $\boldsymbol{\nu}(h_1, h_2, \ldots, h_{m-1}, h_m)$ does not exist.

On the right-hand side of (30) there are additional $(m-1)! - 1$ summands of the type (31), in which the indices $i_1, i_2, \ldots, i_{m-1}$ coincide with $h_1, h_2, \ldots, h_{m-1}$, but in some other order. Then the determinant $\boldsymbol{\nu}(i_1, i_2, \ldots, i_m)(k|m)$ can be brought into the form $\boldsymbol{\nu}(h_1, h_2, \ldots, h_m)(k|m)$ by a number of transpositions of columns of $\boldsymbol{\nu}(i_1, i_2, \ldots, i_m)(k|m)$. Each transposition of two columns of a determinant causes the change of its sign. Consequently, it will be

$$\boldsymbol{\nu}(i_1, i_2, \ldots, i_m)(k|m) = (-1)^p \boldsymbol{\nu}(h_1, h_2, \ldots, h_m)(k|m) , \qquad (32)$$

where p is the number of transpositions required in the mapping

$$(i_1, i_2, \ldots, i_{m-1}) \rightarrow (h_1, h_2, \ldots, h_{m-1}) .$$

As known from algebra, p is just the parity of the permutation $(i_1, i_2, \ldots, i_{m-1})$ relative to $(h_1, h_2, \ldots, h_{m-1})$.

By summing the $(m-1)!$ terms on the right-hand side of (30) in which the indices $i_1, i_2, \ldots, i_{m-1}$ (when appropriately ordered) coincide with $(h_1, h_2, \ldots, h_{m-1})$, by using (32), and by taking into account the definition of a determinant, we obtain

$$\sum_{i_1,\ldots,i_{m-1}} (-1)^p \frac{\nu_{1,i_1}\nu_{2,i_2}\cdots\nu_{j-1,i_{j-1}}\nu_{j+1,i_j}\cdots\nu_{m,i_{m-1}}}{n_{i_1}n_{i_2}\cdots n_{i_{m-1}}} \times \boldsymbol{\nu}(h_1, h_2, \ldots, h_{m-1}, h_m)(k|m)$$
$$= \frac{\boldsymbol{\nu}(h_1, h_2, \ldots, h_{m-1}, h_m)(j|m)\boldsymbol{\nu}(h_1, h_2, \ldots, h_{m-1}, h_m)(k|m)}{n_{h_1}n_{h_2}\cdots n_{h_{m-1}}}. \tag{33}$$

Recall that, by definition, the determinant obeys the relation

$$\begin{vmatrix} a_{11} & a_{12} & \cdots & a_{1p} \\ a_{21} & a_{22} & \cdots & a_{2p} \\ \cdots & & \cdots & \\ a_{p1} & a_{p2} & \cdots & a_{pp} \end{vmatrix} = \sum_{i_1,\ldots,i_p} (-1)^p a_{1,i_1}a_{2,i_2}\cdots a_{p,i_p}.$$

From (33) it immediately follows that

$$\Delta^*(k|j) = \sum_{h_1<h_2<\ldots<h_{m-1}} \frac{\boldsymbol{\nu}(h_1, h_2, \ldots, h_{m-1}, h_m)(j|m)\boldsymbol{\nu}(h_1, h_2, \ldots, h_{m-1}, h_m)(k|m)}{n_{h_1}n_{h_2}\cdots n_{h_{m-1}}},$$

i.e.

$$\Delta^*(k|j) = \sum_{i_1<i_2<\ldots<i_{m-1}} \frac{\boldsymbol{\nu}(i_1, i_2, \ldots, i_{m-1}, i_m)(j|m)\boldsymbol{\nu}(i_1, i_2, \ldots, i_{m-1}, i_m)(k|m)}{n_{i_1}n_{i_2}\cdots n_{i_{m-1}}}.$$

Substitution of the above expression back into (29) yields after a number of pertinent rearrangements,

$$\Lambda_1 = \sum_{i_1<i_2<\ldots<i_{m-1}} \frac{1}{n_{i_1}n_{i_2}\cdots n_{i_{m-1}}} \left[\sum_{j=1}^{m}(-1)^{m+j}\nu_{ji}\boldsymbol{\nu}(j|m)\right] \times \left[\sum_{k=1}^{m}(-1)^{m+k}X_k\boldsymbol{\nu}(k|m)\right]. \tag{34}$$

We now have to observe that the first term in square brackets on the right-hand side of (34) is just the determinant $D(i_1, i_2, \ldots, i_{m-1}, i)$, eq. (9), expanded with respect to its mth column. Similarly, the second term in square brackets is equal to $D(i_1, i_2, \ldots, i_{m-1}, X)$, eq. (10), expanded with respect to its mth column. Bearing these facts in mind, we see that (18) is a straightforward consequence of (34).

Step 3

The expression (19) can be deduced following a pattern of reasoning analogous to that employed in Step 2, but somewhat more complicated. We start with formula (28) and expand the determinant $\Delta^{*}_{j,k}$, eq. (26), with respect to both its jth and kth columns. Next we take into account (22) and use the properties (20) and (21). Then the same procedure as in Step 2, leads after a lengthy calculation to the expression (35), whose form is similar to that of (34):

$$\Lambda_2 = \sum_{i_1 < i_2 < \ldots < i_{m-2}} \frac{1}{n_{i_1} n_{i_2} \ldots n_{i_{m-2}}} \left[\sum_{h=1}^{m} \sum_{\substack{l=1 \\ (l \neq h)}}^{m} (-1)^{h+l-1} X_h \Delta\nu_l \boldsymbol{v}(hl|m, m-1) \right] \times \left[\sum_{j=1}^{m} \sum_{\substack{k=1 \\ (k \neq j)}}^{m} (-1)^{j+k} \nu_{ji} \Delta\nu_k \boldsymbol{v}(jk|m, m-1) \right] . \tag{35}$$

Again, the two terms in square brackets on the right-hand side of (35) are respectively equal to the determinants $D(i_1, i_2, \ldots, i_{m-2}, \Delta\nu, i)$ and $D(i_1, i_2, \ldots, i_{m-2}, \Delta\nu, X)$, eqs. (11) and (12), when these are expanded with respect to their mth and $(m-1)$th columns. Formula (19) follows then immediately from (35).

We thus showed that eqs. (17), (18) and (19) hold, and by this the proof of the identity (13) is completed.

6. An example

To exemplify the above relations we consider the partial oxidation of natural gas (say, CH_4) for the production of synthesis gas ($CO + H_2$) with H_2O and CO_2 as byproducts [6]. We choose the parameter Y to be the temperature T. In this case $X_j = \Delta H_j^0 / RT^2$ (see table 1). The process under consideration may be described, for instance, by the following system if independent reactions:

$$\left. \begin{array}{ll} CH_4 + H_2O = CO + 3H_2 \,, & \Delta\nu_1 = 2, \Delta H_1^0 \\ CH_4 + 2H_2O = CO_2 + 4H_2 \,, & \Delta\nu_2 = 2, \Delta H_2^0 \\ CH_4 + 2O_2 = CO_2 + 2H_2O \,, & \Delta\nu_3 = 0, \Delta H_3^0 \end{array} \right\} \tag{36}$$

At $T = 1000$ K the above standard reaction enthalpies are equal to $\Delta H_1^0 = 225.39$ kJ/mol, $\Delta H_2^0 = 190.62$ kJ/mol and $\Delta H_3^0 = -800.82$ kJ/mol. The stoichiometric matrix for this system reads

$$\begin{array}{cccccc} CH_4 & H_2O & O_2 & CO & CO_2 & H_2 \end{array}$$
$$\left\| \begin{array}{cccccc} -1 & -1 & 0 & 1 & 0 & 3 \\ -1 & -2 & 0 & 0 & 1 & 4 \\ -1 & 2 & -2 & 0 & 1 & 0 \end{array} \right\| .$$

To derive and interpret the sensitivity coefficients we first have to construct the set of all response reactions. In order to obtain the Hessian reactions we have to eliminate $m - 1 = 3 - 1 = 2$ species from the initial set of reactions, eq. (36). if, for instance, the species to be eliminated are CH_4 and H_2O, then the respective HR is

$$\begin{vmatrix} -1 & -1 & 0 \\ -1 & -2 & 0 \\ -1 & 2 & -2 \end{vmatrix} O_2 + \begin{vmatrix} -1 & -1 & 1 \\ -1 & -2 & 0 \\ -1 & 2 & 0 \end{vmatrix} CO + \begin{vmatrix} -1 & -1 & 0 \\ -1 & -2 & 1 \\ -1 & 2 & 1 \end{vmatrix} CO_2$$

$$+ \begin{vmatrix} -1 & -1 & 3 \\ -1 & -2 & 4 \\ -1 & 2 & 0 \end{vmatrix} H_2 = 0 \, ,$$

which is the same as

$$4CO + 2O_2 = 4CO_2 \, .$$

We next calculate the enthalpy change of this HR using eq. (15):

$$\begin{vmatrix} -1 & -1 & \Delta H_1^0 \\ -1 & -2 & \Delta H_2^0 \\ -1 & 2 & \Delta H_3^0 \end{vmatrix} = 4\Delta H_1^0 - 3\Delta H_2^0 - \Delta H_3^0 \, .$$

Repeating this procedure for all pairs of species, we arrive at the following HRs (the eliminated species are indicated in brackets; the right-hand side expressions are the respective enthalpy changes):

1. (CH_4, H_2O)	$4CO + 2O_2 = 4CO_2$	$4\Delta H_1^0 - 3\Delta H_2^0 - \Delta H_3^0$
2. (CH_4, O_2)	$2H_2O + 2CO = 2CO_2 + 2H_2$	$-2\Delta H_1^0 + 2\Delta H_2^0$
3. (CH_4, CO)	$2O_2 + 4H_2 = 4H_2O$	$-\Delta H_2^0 + \Delta H_3^0$
4. (CH_4, CO_2)	$2O_2 + 4H_2 = 4H_2O$	$-\Delta H_2^0 + \Delta H_3^0$
5. (CH_4, H_2)	$4CO + 2O_2 = 4CO_2$	$4\Delta H_1^0 - 3\Delta H_2^0 - \Delta H_3^0$
6. (H_2O, O_2)	$2CH_4 + 2CO_2 = 4CO + 4H_2$	$2\Delta H_1^0 - 4\Delta H_2^0$
7. (H_2O, CO)	$4CH_4 + 4O_2 = 4CO_2 + 8H_2$	$2\Delta H_2^0 + 2\Delta H_3^0$
8. (H_2O, CO_2)	$4CH_4 + 2O_2 = 4CO + 8H_2$	$4\Delta H_1^0 - \Delta H_2^0 + \Delta H_3^0$
9. (H_2O, H_2)	$8CO + 4O_2 = 8CO_2$	$8\Delta H_1^0 - 6\Delta H_2^0 - 2\Delta H_3^0$
10. (O_2, CO)	$2CH_4 + 4H_2O = 2CO_2 + 8H_2$	$2\Delta H_2^0$
11. (O_2, CO_2)	$2CH_4 + 2H_2O = 2CO + 6H_2$	$2\Delta H_1^0$
12. (O_2, H_2)	$2CH_4 + 6CO_2 = 2H_2O + 8CO$	$8\Delta H_1^0 - 6\Delta H_2^0$
13. (CO, CO_2)	$2O_2 + 4H_2 = 4H_2O$	$-\Delta H_2^0 + \Delta H_3^0$
14. (CO, H_2)	$4CH_4 + 8O_2 = 4CO_2 + 8H_2O$	$4\Delta H_3^0$
15. (CO_2, H_2)	$4CH_4 + 6O_2 = 4CO + 8H_2O$	$4\Delta H_1^0 - 3\Delta H_2^0 + 3\Delta H_3^0$

Observe that not all HRs are mutually distinct. In our example this is the case with the reactions 3, 4 and 13, as well as with 1, 5 and 9.

In an analogous way, eliminating only one species from (36), we readily construct the non-Hessian reactions. For example, if the species to be eliminated is CH_4 we have the following NHR:

$$\begin{vmatrix} -1 & 2 & -1 \\ -1 & 2 & -2 \\ -1 & 0 & 0 \end{vmatrix} H_2O + \begin{vmatrix} -1 & 2 & 0 \\ -1 & 2 & 0 \\ -1 & 0 & -2 \end{vmatrix} O_2 + \begin{vmatrix} -1 & 2 & 1 \\ -1 & 2 & 0 \\ -1 & 0 & 0 \end{vmatrix} CO$$

$$+ \begin{vmatrix} -1 & 2 & 0 \\ -1 & 2 & 1 \\ -1 & 0 & 1 \end{vmatrix} CO_2 + \begin{vmatrix} -1 & 2 & 3 \\ -1 & 2 & 4 \\ -1 & 0 & 0 \end{vmatrix} H_2 = 0 \,,$$

which is the same as

$$2H_2O + 2CO = 2CO_2 + 2H_2 \,.$$

The respective enthalpy change is

$$\begin{vmatrix} -1 & 2 & \Delta H_1^0 \\ -1 & 2 & \Delta H_2^0 \\ -1 & 0 & \Delta H_3^0 \end{vmatrix} = -2\Delta H_1^0 + 2\Delta H_2^0 \,.$$

Repeating this procedure for the remaining five species involved in (36), we ultimately arrive at the following NHRs:

1. (CH_4)	$2H_2O + 2CO = 2CO_2 + 2H_2$	$-2\Delta H_1^0 + 2\Delta H_2^0$
2. (H_2O)	$2CH_4 + 4O_2 + 4CO = 6CO_2 + 4H_2$	$-4\Delta H_1^0 + 4\Delta H_2^0 + 2\Delta H_3^0$
3. (O_2)	$4H_2O + 4CO = 4CO_2 + 4H_2$	$-4\Delta H_1^0 + 4\Delta H_2^0$
4. (CO)	$2CH_4 + 4O_2 = 4H_2O + 2CO_2$	$2\Delta H_3^0$
5. (CO_2)	$2CH_4 + 4O_2 + 2H_2 = 6H_2O + 2CO$	$2\Delta H_1^0 - 2\Delta H_2^0 + 2\Delta H_3^0$
6. (H_2)	$2CH_4 + 4O_2 = 4H_2O + 2CO_2$	$2\Delta H_3^0$

As before, not all non-Hessian reactions need to be mutually distinct; in the above list reactions 1 and 3 as well as 4 and 6 coincide.

From these data one can readily derive the sensitivity coefficients. For example, if we are interested in the sensitivity coefficient of CH_4 we have to take into account only those response reactions in which CH_4 is involved. It is seen, that CH_4 is involved in the Hessian reactions 6, 7, 8, 10, 11, 12, 14 and 15. The contribution to the sentivity coefficient from each of these reactions is equal to the product of the stoichiometric coefficient of CH_4 and the enthalpy change of the respective HR, divided by the product of the number of moles of those species which were eliminated. Further, CH_4 is also involved in the non-Hessian reactions 2, 4, 5 and 6. The contribution of each of these reactions is again equal to the product of the stoichiometric coefficient of CH_4 and the enthalpy change of the respective NHR, divided by the product of the total amount of substance and the number of moles of the species which was eliminated. Thus, for the sensitivity coefficient $\partial n_{\mathrm{CH_4}}/\partial T$ we have:

$$\begin{aligned}
\partial n_{\mathrm{CH_4}}/\partial T = -\frac{1}{RT^2\Delta}\Bigg\{ & \frac{2(2\Delta H_1^0 - 4\Delta H_2^0)}{n_{\mathrm{H_2O}} n_{\mathrm{O_2}}} + \frac{4(2\Delta H_2^0 + 2\Delta H_3^0)}{n_{\mathrm{H_2O}} n_{\mathrm{CO}}} \\
& + \frac{4(4\Delta H_1^0 - \Delta H_2^0 + \Delta H_3^0)}{n_{\mathrm{H_2O}} n_{\mathrm{CO_2}}} + \frac{2(2\Delta H_2^0)}{n_{\mathrm{O_2}} n_{\mathrm{CO}}} + \frac{2(2\Delta H_1^0)}{n_{\mathrm{O_2}} n_{\mathrm{CO_2}}} \\
& + \frac{2(8\Delta H_1^0 - 6\Delta H_2^0)}{n_{\mathrm{O_2}} n_{\mathrm{H_2}}} + \frac{4(4\Delta H_3^0)}{n_{\mathrm{CO}} n_{\mathrm{H_2}}} + \frac{4(4\Delta H_1^0 - 3\Delta H_2^0 + 3\Delta H_3^0)}{n_{\mathrm{CO_2}} n_{\mathrm{H_2}}} \\
& + \frac{1}{n_t}\Bigg[\frac{2(-4\Delta H_1^0 + 4\Delta H_2^0 + 2\Delta H_3^0)}{n_{\mathrm{H_2O}}} + \frac{2(2\Delta H_3^0)}{n_{\mathrm{CO}}} \\
& + \frac{2(2\Delta H_1^0 - 2\Delta H_2^0 + 2\Delta H_3^0)}{n_{\mathrm{CO_2}}} + \frac{2(2\Delta H_3^0)}{n_{\mathrm{H_2}}}\Bigg]\Bigg\}.
\end{aligned}$$

7. Discussion

As seen from our main results, eqs. (13) and (16), in the general case the sensitivity coefficients depend on both the Hessian and the non-Hessian reactions. There are, however, a few special cases in which the NHRs need not be considered at all.

(a) If the sum of stoichiometric coefficients in all m chemical reactions (1) is equal to zero, then all entries in the $(m-1)$th column of the determinant $D(i_1, i_2, \ldots, i_{m-2}, \Delta\nu, i)$ are equal to zero, and consequently, $D(i_1, i_2, \ldots, i_{m-2}, \Delta\nu, i) = 0$. This implies that the second summation on the right-hand side of (13) and (16) vanishes, i.e., the non-Hessian reactions have no effect on $\partial n_i/\partial Y$.

(b) If the parameter Y is chosen to be the pressure, then X_j is proportional to $\Delta\nu_j$, see table 1. Then, however, the mth column of the determinant $D(i_1, i_2, \ldots, i_{m-2}, \Delta\nu, X)$ is proportional to the $(m-1)$th column, implying $D(i_1, i_2, \ldots, i_{m-2}, \Delta\nu, X) = 0$. Again, the second summation on the right-hand side of (13) and (16) vanishes and we conclude that the pressure influences the equilibrium only via the Hessian response reactions.

(c) Because of the very same reason also the sensitivity coefficient $\partial n_i/\partial n_z$ does not involve the non-Hessian response reactions.

(d) It is easy to see that

$$\sum_{i=1}^{n} D(i_1, i_2, \ldots, i_{m-2}, \Delta\nu, i) = D(i_1, i_2, \ldots, i_{m-2}, \Delta\nu, \Delta\nu) = 0\,.$$

As a consequence of this, the sum of the sensitivity coefficients over all reacting species, $\sum_{i=1}^{n} \partial n_i/\partial Y$, does not involve the NHRs. This conclusion holds for arbitrary Y. The same applies also to $\partial n_t/\partial Y$, where n_t is the total amount of species in the system considered.

(e) The contributions originating from the non-Hessian reactions can be disregarded also when considering chemical equilibria in diluted solutions. In this case, namely, n_t (including the number of moles of the solvent) is much greater than any n_i. Therefore the numerical value of the last term on the right-hand side of (13) and (16) becomes negligibly small.

In our opinion, the chemically most significant finding of this work is that the sensitivity coefficients can be expressed as linear combinations of contributions originating from certain distinct classes of chemical reactions. The sensitivity coefficients depend in a rather complicated manner on the parameters which govern the chemical equilibria. The analysis elaborated in this paper enables us to gain a deeper insight into this dependence, and to interpret in a chemically meaningful way the increments whose sums the sensitivity coefficients happen to be. These increments are associated with two well-defined types of chemical reactions, namely, Hessian and non-Hessian response reactions. By this the sensitivity analysis of complex chemical equilibria is significantly simplified and we are able to interpret the overall sensitivity in terms of chemical reactions which strictly obey the Le Chatelier principle.

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