

Joule–Thomson coefficient in systems with multiple chemical equilibria

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Multiple chemical equilibria under adiabatic conditions $H, P = \text{const.}$ are considered. It is shown that in this case the Joule–Thomson coefficient may also be expressed in terms of response equilibria, which were previously introduced in the study of equilibria achieved under $T, P = \text{const.}$ Nevertheless, our approach reveals some noteworthy differences between the isothermic and adiabatic equilibria.

1. Introduction

The Joule–Thomson coefficient μ is the change of temperature caused by the change of pressure at constant enthalpy, $\mu = (\partial T / \partial P)_H$. It plays a distinguished role in chemical thermodynamics. (Recall that among the 336 possible first partial derivatives involving the eight common thermodynamic variables, viz., P, V, T, U, H, S, A and G , only μ has been named after scientists.) In view of this we examined the behavior of μ in systems with multiple chemical equilibria, using a recently developed theoretical technique [1–6]. The thermodynamic identities for μ , obtained in this work, seem to be hitherto unknown.

Throughout this paper it is assumed that the system considered is at thermodynamic equilibrium.

Recently the concept of response equilibria in chemical thermodynamics was shown [1–6] to be useful when considering the sensitivity of the equilibrium state of general reacting systems with respect to different parameters influencing the position of the equilibrium. It appears that within the stoichiometric formulation of the equilibrium conditions, the system's response may be presented as a sum of contributions associated with so-called Hessian and non-Hessian response equilibria

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(HEQs and NHEQs), and pairs thereof. For ideal systems the response is given as a sum of contributions originating solely from response equilibria (i.e., without contributions from pairs of HEQs and/or NHEQs). So far, systems at constant temperature and pressure ($T, P = \text{const.}$) have been considered [1–6]. We now extend our approach to systems constrained by constant enthalpy and pressure ($H, P = \text{const.}$), with emphasis on the Joule–Thomson coefficient.

2. Definitions and notation

We consider the general case of a multiple-equilibrium chemical system in which n distinct chemical species, A_1, A_2, \dots, A_n interact in accordance with the following set of stoichiometrically independent reactions (SIRs):

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

Here ν_{ri} ($r = 1, 2, \dots, m, i = 1, 2, \dots, n$) are stoichiometric coefficients assumed, as usual, to be negative for reactants and positive for reaction products. Every SIR is characterized by its extent $\xi_r, r = 1, 2, \dots, m$.

Let n_i^0 and n_i stand for the initial and equilibrium amounts, respectively, of the species $A_i, i = 1, 2, \dots, n$. If an inert species is present in the system, then we denote it by A_{n+1} ; its stoichiometric coefficient $\nu_{r,n+1}$ in any of the SIRs is equal to zero. Then, the following mass-balance conditions are valid:

$$\begin{aligned} n_i &= n_i^0 + \sum_{r=1}^m \nu_{ri} \xi_r, \\ n_t &= \sum_{i=1}^{n+1} n_i = n_t^0 + \sum_{r=1}^m \Delta \nu_r \xi_r. \end{aligned}$$

By $\Delta \nu_r$ is denoted the sum of the stoichiometric coefficients of the r th SIR whereas n_t is the total amount of species.

3. Basic thermodynamic relations

The theory of adiabatic processes in reacting mixtures has been outlined in due detail in many textbooks of chemical thermodynamics (see, in particular, pp. 345–349 in [7]). Under adiabatic constraints the following relations hold at the equilibrium state [7–9]:

$$H = \sum_{i=1}^{n+1} n_i \bar{H}_i = \text{const.}, \quad (2)$$

$$\Delta G_r = \frac{\partial G}{\partial \xi_r} = \sum_{i=1}^n \nu_{ri} \mu_i = 0, \quad r = 1, 2, \dots, m, \quad (3)$$

where \bar{H}_i and μ_i are the partial molar enthalpy and chemical potential, respectively, of the species A_i , and ΔG_r is the change of Gibbs energy in the r th SIR, defined via eq. (3). Eqs. (2) and (3) enable the calculation of both the equilibrium composition $\xi \equiv (\xi_1, \xi_2, \dots, \xi_m)$ and temperature T . Then H and ΔG_r may be viewed as functions of ξ , T and P , i.e., $H = H(\xi_1, \xi_2, \dots, \xi_m, T, P)$ and $\Delta G_r = \Delta G_r(\xi_1, \xi_2, \dots, \xi_m, T, P)$. Consequently,

$$\sum_{s=1}^m \left(\frac{\partial H}{\partial \xi_s} \right)_{T,P} \left(\frac{\partial \xi_s}{\partial P} \right)_H + \left(\frac{\partial H}{\partial T} \right)_{P,\xi} \left(\frac{\partial T}{\partial P} \right)_H + \left(\frac{\partial H}{\partial P} \right)_{T,\xi} = 0, \quad (4)$$

$$\sum_{s=1}^m \left(\frac{\partial \Delta G_r}{\partial \xi_s} \right)_{T,P} \left(\frac{\partial \xi_s}{\partial P} \right)_H + \left(\frac{\partial \Delta G_r}{\partial T} \right)_{P,\xi} \left(\frac{\partial T}{\partial P} \right)_H + \left(\frac{\partial \Delta G_r}{\partial P} \right)_{T,\xi} = 0, \quad (5)$$

$r = 1, 2, \dots, m.$

In chemical thermodynamics it is known that [8]

$$\left(\frac{\partial H}{\partial \xi_r} \right)_{T,P} = \sum_{i=1}^{n+1} \left(\frac{\partial n_i}{\partial \xi_r} \right)_{T,P} \bar{H}_i = \sum_{i=1}^n \nu_{ri} \bar{H}_i = \Delta H_r,$$

$$\left(\frac{\partial H}{\partial T} \right)_{P,\xi} = \sum_{i=1}^{n+1} n_i \left(\frac{\partial \bar{H}_i}{\partial T} \right)_{P,\xi} = \sum_{i=1}^{n+1} n_i \bar{C}_{P,i} = C_{P,\xi},$$

$$\frac{1}{RT} \left(\frac{\partial \Delta G_r}{\partial \xi_s} \right)_{T,P} = \frac{1}{RT} \left(\frac{\partial^2 G}{\partial \xi_r \partial \xi_s} \right)_{T,P} \equiv G_{rs},$$

$$\left(\frac{\partial \Delta G_r}{\partial T} \right)_{P,\xi} = -\frac{\Delta H_r}{T}, \quad \left(\frac{\partial \Delta G_r}{\partial P} \right)_{T,\xi} = \Delta V_r,$$

$$\left(\frac{\partial H}{\partial P} \right)_{T,\xi} = \left[V - T \left(\frac{\partial V}{\partial T} \right)_{P,\xi} \right], \quad (6)$$

where, as usual, ΔH_r and ΔV_r stand for the standard enthalpy and volume change of the r th SIR, whereas $C_{P,\xi}$ and V are the heat capacity and volume of the equilibrium mixture. Observe that the quantity G_{rs} is defined by means of eq. (6). Now, eqs. (4) and (5) are transformed into

$$\left(\frac{\partial T}{\partial P}\right)_H = -\frac{1}{C_{P,\xi}} \left[\left[V - T \left(\frac{\partial V}{\partial T}\right)_{P,\xi} \right] + \sum_{s=1}^m \Delta H_s \left(\frac{\partial \xi_s}{\partial P}\right)_H \right] \quad (7)$$

and

$$\sum_{s=1}^m G_{rs} \left(\frac{\partial \xi_s}{\partial P}\right)_H - \frac{\Delta H_r}{RT^2} \left(\frac{\partial T}{\partial P}\right)_H = -\frac{1}{RT} \Delta V_r, \quad r = 1, 2, \dots, m. \quad (8)$$

The quantity appearing on the left-hand side of eq. (7) is just the Joule–Thomson coefficient μ . We see that is composed of two terms, which we refer to as non-chemical and chemical.

$$\mu = \mu^{\text{nc}} + \mu^{\text{ch}},$$

$$\mu^{\text{nc}} = -\frac{1}{C_{p,\xi}} \left[V - T \left(\frac{\partial V}{\partial T}\right)_{P,\xi} \right], \quad (9)$$

$$\mu^{\text{ch}} = -\frac{1}{C_{p,\xi}} \sum_{s=1}^m \Delta H_s \left(\frac{\partial \xi_s}{\partial P}\right)_H. \quad (10)$$

Clearly, in the absence of chemical reactions between the species present in the system, the Joule–Thomson coefficient is equal to μ^{nc} . The chemical equilibria, eqs. (1), induce an additional contribution to μ , expressed via eq. (10). We readily recognize that

$$-\frac{1}{C_{p,\xi}} \Delta H_s (\partial \xi_s / \partial P)_H$$

is the increment to μ^{ch} pertaining to the s th SIR, $s = 1, 2, \dots, m$. If $m > 1$, then the SIRs, eqs. (1), can be chosen in infinitely many ways, to be all stoichiometrically equivalent. Therefore, the decomposition of μ^{ch} into contributions coming from individual SIRs is not unique and the selection of the terms

$$-\frac{1}{C_{p,\xi}} \Delta H_s (\partial \xi_s / \partial P)_H$$

is to a great degree arbitrary. This difficulty will be overcome by decomposing μ^{ch} into increments associated with response equilibria and pairs thereof.

In what follows we will be mainly interested in the chemical component of the Joule–Thomson coefficient, μ^{ch} , eq. (10).

The motivation for the above specified terminology is that the “chemical” term, eq. (10), in an evident and explicit manner depends on the chemical reactions occurring in the system. Not able to find a more appropriate name, we call the other term, eq. (9), “non-chemical”. It should, however, be noticed that the volume (V) in eq. (9) is a function of both T , P as well as reaction extents ξ_1 , ξ_2 ,

..., ξ_m . Thus, the specification “non-chemical” (which, anyway, is just a name) does not mean that μ^{nc} is claimed to be independent of the chemical processes occurring in the system. (At this point we also wish to make clear that the present partition of the Joule–Thomson coefficient into μ^{nc} and μ^{ch} differs from the usual [7–9] partition of thermodynamic partial derivatives into a contribution coming from a “frozen” mixture of species [8] – which is strictly reaction-independent – and the reaction-dependent “configurational” [8] or “relaxational” [10] contribution.)

Substituting eq. (7) into eq. (8) we arrive at the following system of m linear equations in m unknowns $(\partial\xi_s/\partial P)_H, s = 1, 2, \dots, m$:

$$\begin{aligned} L_{11} \frac{\partial\xi_1}{\partial P} + L_{12} \frac{\partial\xi_2}{\partial P} + \dots + L_{1m} \frac{\partial\xi_m}{\partial P} &= \Lambda_1, \\ L_{21} \frac{\partial\xi_1}{\partial P} + L_{22} \frac{\partial\xi_2}{\partial P} + \dots + L_{2m} \frac{\partial\xi_m}{\partial P} &= \Lambda_2, \\ \dots & \dots \dots \dots \dots \\ L_{m1} \frac{\partial\xi_1}{\partial P} + L_{m2} \frac{\partial\xi_2}{\partial P} + \dots + L_{mm} \frac{\partial\xi_m}{\partial P} &= \Lambda_m, \end{aligned} \quad (11)$$

where

$$L_{rs} = G_{rs} + b\Delta H_r\Delta H_s, \quad b = \frac{1}{C_{p,\xi}RT^2}, \quad (12)$$

$$\Lambda_r = - \left[\frac{1}{RT} \Delta V_r + b\Delta H_r \left[V - T \left(\frac{\partial V}{\partial T} \right)_{P,\xi} \right] \right]. \quad (13)$$

The solution of the system (11) is

$$\left(\frac{\partial\xi_s}{\partial P} \right)_H = \frac{(\Delta_s)_{H,P}}{\Delta_{H,P}}; \quad s = 1, 2, \dots, m, \quad (14)$$

where

$$\Delta_{H,P} = \det\|L_{rs}\| = \begin{vmatrix} L_{11} & L_{12} & \dots & L_{1m} \\ L_{21} & L_{22} & \dots & L_{2m} \\ \vdots & \vdots & & \vdots \\ L_{m1} & L_{m2} & \dots & L_{mm} \end{vmatrix}, \quad (15)$$

$$(\Delta_s)_{H,P} = \begin{vmatrix} L_{11} & L_{12} & \cdots & L_{1,s-1} & \Lambda_1 & L_{1,s+1} & \cdots & L_{1m} \\ L_{21} & L_{22} & \cdots & L_{2,s-1} & \Lambda_2 & L_{2,s+1} & \cdots & L_{2m} \\ \vdots & \vdots & & \vdots & \vdots & \vdots & & \vdots \\ L_{m1} & L_{m2} & \cdots & L_{m,s-1} & \Lambda_m & L_{m,s+1} & \cdots & L_{mm} \end{vmatrix}.$$

Substituting eq. (14) into eq. (10) we obtain our starting expression for the (chemical component of the) Joule–Thomson coefficient:

$$\mu^{\text{ch}} = -\frac{1}{C_{p,\xi}\Delta_{H,P}} \sum_{s=1}^m \Delta H_s (\Delta_s)_{H,P}. \quad (16)$$

If the model of the system under consideration is specified (ideal behavior, for instance), then eq. (7) permits a quantitative evaluation of the Joule–Thomson coefficient. In the case of multiple equilibria, however, the Joule–Thomson coefficient is quite complex and its qualitative behavior cannot be predicted from eq. (7) (without performing numerical calculations) even in the case of ideal systems. Recall that in ideal systems $\mu^{\text{nc}} = 0$. One of the ways to simplify the treatment of the Joule–Thomson coefficient and to make its behavior more transparent is to present μ^{ch} in terms of contributions associated with response equilibria.

4. More notations and definitions

In order to introduce the concept of response equilibria [1–6], recall that the chemical potential μ_i of the species A_i may be considered as a function of the extent of reactions $\mu_i(\xi_1, \xi_2, \dots, \xi_m, T, P)$, or as a function of the number of moles $\mu_i(n_1, n_2, \dots, n_n, n_{n+1}, T, P)$, or as a function of mole fractions $\mu_i(x_1, x_2, \dots, x_n, x_{n+1}, T, P)$. In view of this, we define three matrices:

$$\mathbf{G} = \|G_{ij}\|, \quad G_{ij} = \frac{1}{RT} \sum_{r=1}^n \nu_{jr} \frac{\partial \mu_r}{\partial \xi_i} = \frac{1}{RT} \left(\frac{\partial^2 G}{\partial \xi_i \partial \xi_j} \right), \quad i, j = 1, 2, \dots, m,$$

$$\mathbf{R} = \|R_{ij}\|, \quad R_{ij} = \frac{1}{RT} \frac{\partial \mu_i}{\partial n_j} = \frac{1}{RT} \left(\frac{\partial^2 G}{\partial n_i \partial n_j} \right), \quad i, j = 1, 2, \dots, n+1,$$

$$\mathbf{P} = \|P_{ij}\|, \quad P_{ij} = \frac{1}{RT} \frac{\partial \mu_i}{\partial x_j} = \frac{1}{RT} \left(\frac{\partial^2 G}{\partial n_i \partial x_j} \right), \quad i, j = 1, 2, \dots, n+1.$$

These matrices are interrelated [4,6] as

$$G_{ij} = \sum_{r=1}^n \sum_{s=1}^n \nu_{ir} \nu_{js} R_{rs}, \quad i, j = 1, 2, \dots, m, \quad (17)$$

$$R_{ij} = \frac{1}{n_t} (P_{ij} - a), \quad i, j = 1, 2, \dots, n, \quad (18)$$

where

$$a = \sum_{r=1}^{n+1} \sum_{s=1}^{n+1} x_r x_s P_{rs}.$$

Notice that the summation in eq. (17) is only until $r, s = n$, because $\nu_{i,n+1} = 0$ for all $i = 1, 2, \dots, m$.

Further, consider two ordered sets of integers: an $(m - 1)$ -tuple i_1, i_2, \dots, i_{m-1} , satisfying the condition $1 \leq i_1 < i_2 < \dots < i_{m-1} \leq n$, and an $(m - 2)$ -tuple i_1, i_2, \dots, i_{m-2} , satisfying the condition $1 \leq i_1 < i_2 < \dots < i_{m-2} \leq n$. For them we use the shorthand notion $[i]$ and $\{i\}$, respectively. We then define the following determinants:

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

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

$$D(\{i\}, k) = \begin{vmatrix} \nu_{1,i_1} & \nu_{1,i_2} & \cdots & \nu_{1,i_{m-2}} & \Delta\nu_1 & \nu_{1,k} \\ \nu_{2,i_1} & \nu_{2,i_2} & \cdots & \nu_{2,i_{m-2}} & \Delta\nu_2 & \nu_{2,k} \\ \vdots & \vdots & & \vdots & \vdots & \vdots \\ \nu_{m,i_1} & \nu_{m,i_2} & \cdots & \nu_{m,i_{m-2}} & \Delta\nu_m & \nu_{m,k} \end{vmatrix}, \quad (20)$$

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

These determinants have a definite chemical meaning. Namely, $D([i], k)$ and $D(\{i\}, k)$ are the stoichiometric coefficients of the species A_k in two special classes of reactions, or equilibria, named Hessian response equilibria, HEQs, and non-

Hessian response equilibria, NHEQs, respectively [1–6]. The stoichiometric equation of an HEQ is, thus, given by

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

whereas the stoichiometric equation of an NHEQ reads

$$\sum_{k=1}^n D(\{i\}, k) A_k = 0.$$

It follows that any selection of $m - 1$ species $A_{i_1}, A_{i_2}, \dots, A_{i_{m-1}}$ from a total of n species defines a particular HEQ. We denote this HEQ by $\mathcal{H}(i_1, i_2, \dots, i_{m-1})$ or $\mathcal{H}([i])$ or simply by \mathcal{H} . An NHEQ is defined by a selection of $m - 2$ species $A_{i_1}, A_{i_2}, \dots, A_{i_{m-2}}$ and is denoted by $\mathcal{N}(i_1, i_2, \dots, i_{m-2})$ or $\mathcal{N}(\{i\})$ or simply by \mathcal{N} .

Response equilibria have the following properties. The stoichiometric coefficients of the species $A_{i_1}, A_{i_2}, \dots, A_{i_{m-1}}$ in the HEQ $\mathcal{H}([i])$ and of the species $A_{i_1}, A_{i_2}, \dots, A_{i_{m-2}}$ in the NHEQ $\mathcal{N}(\{i\})$ are equal to zero. The sum of stoichiometric coefficients of a NHEQ is equal to zero. If X_r is a quantity associated with the r th SIR, then $D([i], X)$ and $D(\{i\}, X)$ are the same quantities associated with the HEQ $\mathcal{H}([i])$ and with the NHEQ $\mathcal{N}(\{i\})$, respectively. When misunderstanding is to be avoided, we denote them by $X(\mathcal{H})$ and $X(\mathcal{N})$, respectively. In particular, $\Delta H(\mathcal{H}) = D([i], \Delta H)$ and $\Delta H(\mathcal{N}) = D(\{i\}, \Delta H)$ represent the standard enthalpy changes of $\mathcal{H}([i])$ and $\mathcal{N}(\{i\})$, respectively.

Finally, we define

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

$$\mathbf{R} \begin{pmatrix} [i] \\ [j] \end{pmatrix} = \begin{vmatrix} R_{i_1 j_1} & R_{i_1 j_2} & \cdots & R_{i_1 j_{m-1}} \\ R_{i_2 j_1} & R_{i_2 j_2} & \cdots & R_{i_2 j_{m-1}} \\ \vdots & \vdots & & \vdots \\ R_{i_{m-1} j_1} & R_{i_{m-1} j_2} & \cdots & R_{i_{m-1} j_{m-1}} \end{vmatrix}, \quad (21)$$

$$\mathbf{P} \begin{pmatrix} [i] \\ [j] \end{pmatrix} = \begin{vmatrix} P_{i_1 j_1} & P_{i_1 j_2} & \cdots & P_{i_1 j_{m-1}} \\ P_{i_2 j_1} & P_{i_2 j_2} & \cdots & P_{i_2 j_{m-1}} \\ \vdots & \vdots & & \vdots \\ P_{i_{m-1} j_1} & P_{i_{m-1} j_2} & \cdots & P_{i_{m-1} j_{m-1}} \end{vmatrix},$$

$$\mathbf{P} \begin{pmatrix} \{i\} \\ \{j\} \end{pmatrix} = \begin{vmatrix} P_{i_1,j_1} & P_{i_1,j_2} & \cdots & P_{i_1,j_{m-2}} \\ P_{i_2,j_1} & P_{i_2,j_2} & \cdots & P_{i_2,j_{m-2}} \\ \vdots & \vdots & & \vdots \\ P_{i_{m-2},j_1} & P_{i_{m-2},j_2} & \cdots & P_{i_{m-2},j_{m-2}} \end{vmatrix}. \quad (22)$$

The above determinants were shown to represent the extent of coupling between HEQs (the first two) and NHEQs (the third one) [4,6].

5. The main results

We are now in a position to formulate the following results:

$$\Delta_{H,P} = \Delta_{T,P} + b \sum_{[i]} \sum_{[j]} \mathbf{R} \begin{pmatrix} [i] \\ [j] \end{pmatrix} D([i], \Delta H) D([j], \Delta H), \quad (23)$$

where

$$\Delta_{T,P} = \frac{1}{m} \sum_{[i]} \sum_{[j]} \mathbf{R} \begin{pmatrix} [i] \\ [j] \end{pmatrix} L([i], [j]) \quad (24)$$

and

$$\mu^{\text{ch}} = -\frac{1}{C_{p,\xi} \Delta_{H,P}} \sum_{[i]} \sum_{[j]} \mathbf{R} \begin{pmatrix} [i] \\ [j] \end{pmatrix} D([i], \Lambda) D([j], \Delta H), \quad (25)$$

$$\begin{aligned} \mu^{\text{ch}} = & -\frac{1}{C_{p,\xi} \Delta_{H,P} n_i^{m-1}} \left[\sum_{[i]} \sum_{[j]} \mathbf{P} \begin{pmatrix} [i] \\ [j] \end{pmatrix} D([i], \Lambda) D([j], \Delta H), \right. \\ & \left. - a \sum_{\{i\}} \sum_{\{j\}} \mathbf{P} \begin{pmatrix} \{i\} \\ \{j\} \end{pmatrix} D(\{i\}, \Lambda) D(\{j\}, \Delta H) \right]. \quad (26) \end{aligned}$$

The proof of these results is given in the appendix.

The fundamental feature of the above formulas is that they enable us to express both the determinant $\Delta_{H,P}$ and the (chemical component of the) Joule–Thomson coefficient in terms of response reactions. The decomposition of μ into contributions associated with response equilibria is unique and is independent of the choice of SIRs.

There exist two equivalent formulas for the Joule–Thomson coefficient. In eq. (25) the chemical component of the Joule–Thomson coefficient is given as a sum of contributions originating solely from HEQs and pairs thereof. In what follows, the analysis based on eq. (25) will be referred to as the HEQ-approach.

Alternatively, we can represent μ^{ch} in terms of both HEQs and NHEQs,

eq. (26). In this case we speak about the HEQ/NHEQ-approach. Notice that in the HEQ/NHEQ-approach no pairwise interaction between HEQs and NHEQs are encountered.

6. Ideal systems

At a first glance it may look that the HEQ-approach is more advantageous, because eq. (25) contains fewer terms than eq. (26). This, however, is not so, at least not for ideal-gas-phase adiabatic processes. Indeed, in this case the HEQ-approach leads to non-zero pair-contributions [4]. A way to avoid pair-contributions is to rearrange the system’s response so as to introduce NHEQs, which is tantamount to the HEQ/NHEQ-approach. In view of this we restrict our discussion only to the HEQ/NHEQ-approach.

For ideal systems, $\mu^{nc} = 0$ because of [9]

$$V - T \left(\frac{\partial V}{\partial T} \right)_{P,\xi} = 0 \tag{27}$$

and, consequently, $\mu = \mu^{ch}$. For ideal systems, we further have

$$\mu_i = \mu_i^0 + RT \ln x_i, \quad P_{rs} = \frac{\delta_{rs}}{x_s}, \quad a = 1,$$

where δ_{rs} is the Kronecker delta. This implies [3,6]

$$\mathbf{P} \left(\begin{matrix} [i] \\ [j] \end{matrix} \right) = \frac{1}{x_{i_1} x_{i_2} \dots x_{i_{m-1}}} \delta_{[i],[j]} = \frac{n_i^{m-1}}{n_{i_1} n_{i_2} \dots n_{i_{m-1}}} \delta_{[i],[j]},$$

$$\mathbf{P} \left(\begin{matrix} \{i\} \\ \{j\} \end{matrix} \right) = \frac{1}{x_{i_1} x_{i_2} \dots x_{i_{m-2}}} \delta_{\{i\},\{j\}} = \frac{n_i^{m-2}}{n_{i_1} n_{i_2} \dots n_{i_{m-2}}} \delta_{\{i\},\{j\}}.$$

From eq. (26) is now seen that in ideal systems contributions to μ , coming from pairs of HEQs and pairs of NHEQs vanish. Consequently, the system’s response is equal to a sum of contributions coming only from individual response equilibria:

$$\mu = - \frac{1}{C_{p,\xi} \Delta H,P} \left[\sum_{\mathcal{H}} \pi(\mathcal{H}) \Lambda(\mathcal{H}) \Delta H(\mathcal{H}) - \sum_{\mathcal{N}} \pi(\mathcal{N}) \Lambda(\mathcal{N}) \Delta H(\mathcal{N}) \right], \tag{28}$$

where

$$\pi(\mathcal{H}) = (n_{i_1} n_{i_2} \dots n_{i_{m-1}})^{-1}, \quad \pi(\mathcal{N}) = (n_{i_1} n_{i_2} \dots n_{i_{m-2}} n_t)^{-1}.$$

In view of eq. (27), eq. (13) is reduced to

$$\Lambda_r = -\frac{\Delta\nu_r}{P}, \quad r = 1, 2, \dots, m. \quad (29)$$

Inserting eq. (29) into eq. (28) and taking into account

$$\Lambda(\mathcal{H}) = D([i], \Lambda) = -\frac{1}{P} D([i], \Delta\nu) = -\frac{1}{P} \Delta\nu(\mathcal{H}),$$

$$\Lambda(\mathcal{N}) = D(\{i\}, \Lambda) = -\frac{1}{P} D(\{i\}, \Delta\nu) = -\frac{1}{P} \Delta\nu(\mathcal{N}) = 0,$$

we obtain

$$\mu = \frac{1}{PC_{p,\xi}\Delta H_{H,P}} \sum_{\mathcal{H}} \pi(\mathcal{H}) \Delta\nu(\mathcal{H}) \Delta H(\mathcal{H}), \quad (30)$$

where $\Delta\nu(\mathcal{H})$ is the sum of stoichiometric coefficients of the respective HEQ. Hence, for ideal systems the Joule–Thomson coefficient is expressed as a sum of contributions coming solely from individual HEQs. As $\pi(\mathcal{H}) > 0$, the sign of these contributions is determined by the sign of the product $\Delta\nu(\mathcal{H}) \cdot \Delta H(\mathcal{H})$.

7. An example

We consider here the effect of pressure on the equilibrium explosion temperature of a mixture of hydrogen and oxygen. This system may be described by the following SIRs:

1. $2\text{H} = \text{H}_2, \quad \Delta H_1 = -457.2 \text{ kJ/mol.}$
2. $2\text{O} = \text{O}_2, \quad \Delta H_2 = -510.7 \text{ kJ/mol.}$
3. $\text{H} + \text{O} = \text{OH}, \quad \Delta H_3 = -447.8 \text{ kJ/mol.}$
4. $2\text{H} + \text{O} = \text{H}_2\text{O}, \quad \Delta H_4 = -965.2 \text{ kJ/mol.}$

The above reaction enthalpies refer to 3000 K. The respective stoichiometric matrix is

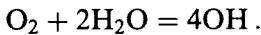
$$\begin{array}{cccccc} \text{H} & \text{O} & \text{H}_2 & \text{O}_2 & \text{OH} & \text{H}_2\text{O} \\ \left| \begin{array}{cccccc} -2 & 0 & 1 & 0 & 0 & 0 \\ 0 & -2 & 0 & 1 & 0 & 0 \\ -1 & -1 & 0 & 0 & 1 & 0 \\ -2 & -1 & 0 & 0 & 0 & 1 \end{array} \right| . \end{array}$$

As $m = 4$, each HEQ is defined by choosing $m - 1 = 3$ species from a total of 6

species. This can be done in 20 distinct ways, resulting in 20 HEQs. If the species selected are H, O and H₂ then the respective HEQ is

$$\begin{aligned} & \begin{vmatrix} -2 & 0 & 1 & -2 \\ 0 & -2 & 0 & 0 \\ -1 & -1 & 0 & -1 \\ -2 & -1 & 0 & -2 \end{vmatrix} \text{H} + \begin{vmatrix} -2 & 0 & 1 & 0 \\ 0 & -2 & 0 & -2 \\ -1 & -1 & 0 & -1 \\ -2 & -1 & 0 & -1 \end{vmatrix} \text{O} \\ & + \begin{vmatrix} -2 & 0 & 1 & 1 \\ 0 & -2 & 0 & 0 \\ -1 & -1 & 0 & 0 \\ -2 & -1 & 0 & 0 \end{vmatrix} \text{H}_2 + \begin{vmatrix} -2 & 0 & 1 & 0 \\ 0 & -2 & 0 & 1 \\ -1 & -1 & 0 & 0 \\ -2 & -1 & 0 & 0 \end{vmatrix} \text{O}_2 \\ & + \begin{vmatrix} -2 & 0 & 1 & 0 \\ 0 & -2 & 0 & 0 \\ -1 & -1 & 0 & 1 \\ -2 & -1 & 0 & 0 \end{vmatrix} \text{OH} + \begin{vmatrix} -2 & 0 & 1 & 0 \\ 0 & -2 & 0 & 0 \\ -1 & -1 & 0 & 0 \\ -2 & -1 & 0 & 1 \end{vmatrix} \text{H}_2\text{O} = 0, \end{aligned}$$

which is equivalent to



The enthalpy change for this HEQ is

$$\begin{vmatrix} -2 & 0 & 1 & \Delta H_1 \\ 0 & -2 & 0 & \Delta H_2 \\ -1 & -1 & 0 & \Delta H_3 \\ -2 & -1 & 0 & \Delta H_4 \end{vmatrix} = -\Delta H_2 + 4\Delta H_3 - 2\Delta H_4.$$

A complete list of HEQs obtained in this way, together with their enthalpy changes at $T = 3000$ K and sums of stoichiometric coefficients is given as follows (only distinct HEQs are given):

	$\Delta H(3000 \text{ K})$ (kJ/mol)	$\Delta \nu$
1. $\text{O}_2 + 2\text{H}_2\text{O} = 4\text{OH}$	649.9	+1
2. $\text{H}_2 + 2\text{OH} = 2\text{H}_2\text{O}$	-577.9	-1
3. $2\text{H}_2 + \text{O}_2 = \text{H}_2\text{O}$	-505.2	-1
4. $\text{H}_2 + \text{O}_2 = 2\text{OH}$	72.3	0
5. $\text{O} + \text{H}_2\text{O} = 2\text{OH}$	69.6	0
6. $2\text{O} = \text{O}_2$	-510.7	-1 (occurs 4 times)
7. $\text{O} + \text{H}_2 = \text{H}_2\text{O}$	-508.0	-1
8. $2\text{O} + 2\text{H}_2 = 2\text{OH}$	-438.4	-1
9. $\text{H} + \text{OH} = \text{H}_2\text{O}$	-517.4	-1
10. $4\text{H} + \text{O}_2 = 2\text{H}_2\text{O}$	-1418.8	-3

11. $2\text{H} + \text{O}_2 = 2\text{OH}$	-384.9	-1
12. $2\text{H} = \text{H}_2$	-457.2	-1 (occurs 4 times)
13. $2\text{H} + \text{O} = \text{H}_2\text{O}$	-965.2	-2
14. $\text{H} + \text{O} = \text{OH}$	-447.8	-1

On the basis of these data we can readily analyze the sign of the Joule–Thomson coefficient, i.e., the effect of pressure on the equilibrium temperature. Indeed, the product $\Delta\nu(\mathcal{H}) \cdot \Delta H(\mathcal{H})$ is positive for all HEQs. From eq. (30) it then follows that $\mu > 0$, i.e., an increase of pressure in this system leads under all circumstances to an increase of temperature. This conclusion is confirmed by numerical calculations¹ shown in Fig. 1.

8. Discussion and concluding remarks

The present analysis shows that the concept of response reactions may be in a natural manner extended to equilibria achieved under conditions different from P , $T = \text{const}$. In particular the Joule–Thomson coefficient, which is an important characteristic of the adiabatic processes (H , $P = \text{const}$), is now shown to be expressible as a sum of contributions coming from response reactions. There exist two distinct, but equivalent, methods of decomposing the Joule–Thomson coefficient in general systems – the HEQ- and the HEQ/NHEQ-approach. Within the HEQ-approach the Gibbs energy is viewed as an implicit function (through the extent of the reaction [12]) of the number of moles of the reacting species. Then the Joule–Thomson coefficient is expressed in terms of HEQs only. When the Gibbs energy of the system is considered as an implicit function of the mole fractions of the reacting species, we arrive at an expression in which the Joule–Thomson coefficient is presented as a sum of contributions coming from HEQs and NHEQs. This is the HEQ/NHEQ-approach.

The interrelation between these two equivalent approaches is best seen when considering ideal systems. In this case the contributions coming from NHEQs are equal to zero. Eqs. (25) and (26), however, are still different. The point is that the function $\mathbf{R} \begin{pmatrix} [i] \\ [j] \end{pmatrix}$ in eq. (25) does not necessarily vanish for $[i] \neq [j]$ and, consequently, in the HEQ-approach, the coupling between HEQs remains even in ideal systems. This is not the case in the HEQ/NHEQ-approach, eq. (26). For ideal systems, we have $\mathbf{P} \begin{pmatrix} [i] \\ [j] \end{pmatrix} = 0$ for $[i] \neq [j]$ and, hence, no coupling. We, therefore, conclude that the HEQ/NHEQ-approach is a way to avoid coupling between response reactions in ideal systems.

¹ Numerical calculations were carried out using ECHIMAD-P/V computer program [11], running on IBM compatible PCs, available on request from one of the authors (D.G.).

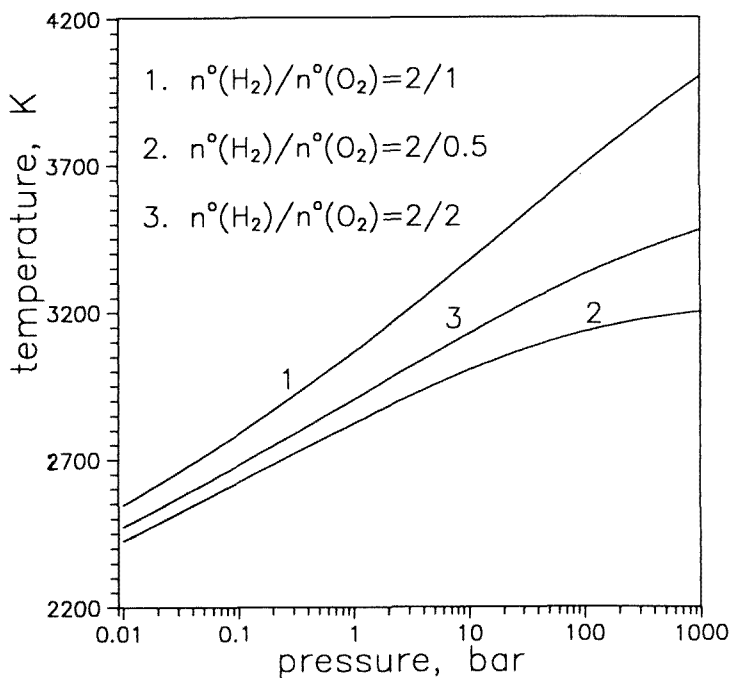


Fig. 1. Equilibrium explosion temperature as a function of pressure for different stoichiometric ratios of hydrogen and oxygen; the initial temperature is taken to be 298 K.

The analysis in this paper was limited to the Joule–Thomson coefficient $(\partial T/\partial P)_H$. Evidently, this partial derivative is just one of the sensitivity coefficients of the system examined. The problem may be readily generalized by considering the sensitivity coefficients pertaining to an arbitrary parameter Y that influences the position of the chemical equilibrium under adiabatic constraints H , $P = \text{const.}$ (as well as under any other thermodynamic constraints [9]). However, a general treatment of the sensitivity coefficients $(\partial T/\partial Y)_{H,P}$ and $(\partial n_k/\partial Y)_{H,P}$ shows that in addition to contributions coming from response reactions there appear additional terms whose meaning is not yet entirely clear. Work along this line is in progress.

Acknowledgements

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Appendix

The proofs of the thermodynamic identities reported in this work are similar to the earlier communicated proofs of some other results in sensitivity analysis of systems with multiple chemical equilibria. In view of this, we skip all steps which can be found in our previous publications. In such cases, the place where the respective algebraic transformations are outlined in due detail is precisely indicated.

Proof of eq. (23)

Substituting eq. (12) into the first column of the determinant $\Delta_{H,P}$, eq. (15), we obtain

$$\begin{aligned} \Delta_{H,P} &= \begin{vmatrix} G_{11} + b \cdot \Delta H_1 \cdot \Delta H_1 & L_{12} & L_{13} & \cdots & L_{1m} \\ G_{21} + b \cdot \Delta H_2 \cdot \Delta H_1 & L_{22} & L_{23} & \cdots & L_{2m} \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ G_{m1} + b \cdot \Delta H_m \cdot \Delta H_1 & L_{m2} & L_{m3} & \cdots & L_{mm} \end{vmatrix}, \\ &= \begin{vmatrix} G_{11} & L_{12} & L_{13} & \cdots & L_{1m} \\ G_{21} & L_{22} & L_{23} & \cdots & L_{2m} \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ G_{m1} & L_{m2} & L_{m3} & \cdots & L_{mm} \end{vmatrix} + b\Delta H_1 \begin{vmatrix} \Delta H_1 & L_{12} & L_{13} & \cdots & L_{1m} \\ \Delta H_2 & L_{22} & L_{23} & \cdots & L_{2m} \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ \Delta H_m & L_{m2} & L_{m3} & \cdots & L_{mm} \end{vmatrix}. \end{aligned}$$

Repeating the same treatment with the second column.

$$\begin{aligned} \Delta_{H,P} &= \begin{vmatrix} G_{11} & G_{12} & L_{13} & \cdots & L_{1m} \\ G_{21} & G_{22} & L_{23} & \cdots & L_{2m} \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ G_{m1} & G_{m2} & L_{m3} & \cdots & L_{mm} \end{vmatrix} + b\Delta H_2 \begin{vmatrix} G_{11} & \Delta H_1 & L_{13} & \cdots & L_{1m} \\ G_{21} & \Delta H_2 & L_{23} & \cdots & L_{2m} \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ G_{m1} & \Delta H_m & L_{m3} & \cdots & L_{mm} \end{vmatrix}, \\ &+ b\Delta H_1 \begin{vmatrix} \Delta H_1 & G_{12} & L_{13} & \cdots & L_{1m} \\ \Delta H_2 & G_{22} & L_{23} & \cdots & L_{2m} \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ \Delta H_m & G_{m2} & L_{m3} & \cdots & L_{mm} \end{vmatrix} \\ &+ b^2 \Delta H_1 \Delta H_2 \begin{vmatrix} \Delta H_1 & \Delta H_1 & L_{13} & \cdots & L_{1m} \\ \Delta H_2 & \Delta H_2 & L_{23} & \cdots & L_{2m} \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ \Delta H_m & \Delta H_m & L_{m3} & \cdots & L_{mm} \end{vmatrix}, \end{aligned}$$

we observe that the last determinant is equal to zero. Continuing the procedure for all columns of $\Delta_{H,P}$, we ultimately arrive at

$$\Delta_{H,P} = \begin{vmatrix} G_{11} & G_{12} & G_{13} & \cdots & G_{1m} \\ G_{21} & G_{22} & G_{23} & \cdots & G_{2m} \\ \vdots & \vdots & \vdots & & \vdots \\ G_{m1} & G_{m2} & G_{m3} & \cdots & G_{mm} \end{vmatrix} + b \sum_{j=1}^m \Delta H_j \begin{vmatrix} G_{11} & G_{12} & \cdots & G_{1,j-1} & \Delta H_1 & G_{1,j+1} & \cdots & G_{1m} \\ G_{21} & G_{22} & \cdots & G_{2,j-1} & \Delta H_2 & G_{2,j+1} & \cdots & G_{2m} \\ \vdots & \vdots & & \vdots & \vdots & & & \vdots \\ G_{m1} & G_{m2} & \cdots & G_{m,j-1} & \Delta H_m & G_{m,j+1} & \cdots & G_{mm} \end{vmatrix}. \quad (\text{A.1})$$

The first term on the right-hand side of eq. (A1) is just the Hessian determinant of the Gibbs energy [1]. In our previous works we denoted it by Δ . Here we denote it by $\Delta_{T,P}$ in order to distinguish it from the determinant $\Delta_{H,P}$. In the theory of isothermic-isobaric chemical equilibria $\Delta_{T,P}$ plays the same role as does $\Delta_{H,P}$ in the theory of chemical equilibria under the constraints $H, P = \text{const}$.

Eq. (24) is just “Result 1” stated and demonstrated in ref. [4].

In order to complete the proof of eq. (23) it remains to show that

$$\sum_{j=1}^m \Delta H_j \begin{vmatrix} G_{11} & \cdots & G_{1,j-1} & \Delta H_1 & G_{1,j+1} & \cdots & G_{1m} \\ G_{21} & \cdots & G_{2,j-1} & \Delta H_2 & G_{2,j+1} & \cdots & G_{2m} \\ \vdots & & \vdots & \vdots & & & \vdots \\ G_{m1} & \cdots & G_{m,j-1} & \Delta H_m & G_{m,j+1} & \cdots & G_{mm} \end{vmatrix} = \sum_{[i]} \sum_{[j]} \mathbf{R} \left(\begin{matrix} [i] \\ [j] \end{matrix} \right) D([i], \Delta H) D([j], \Delta H). \quad (\text{A.2})$$

The proof of eq. (A.2) follows precisely the same lines as the proof of “Result 2” in ref. [4]. The only difference is that instead of ΔH_j we earlier [4] had ν_{jk} and that the j th column in the determinant occurring on the left-hand side of eq. (A.2) earlier [4] contained a variable denoted by X .

Proof of eq. (25)

We start with eq. (16) and consider the sum occurring on its right-hand side. By means of a reasoning fully analogous to what was used above to obtain eq. (A.1), we get

$$\sum_{s=1}^m \Delta H_s(\Delta_s)_{H,P} = \sum_{s=1}^m \Delta H_s \left\{ \begin{array}{cccccc} G_{11} & \cdots & G_{1,s-1} & \Lambda_1 & G_{1,s+1} & \cdots & G_{1m} \\ G_{21} & \cdots & G_{2,s-1} & \Lambda_2 & G_{2,s+1} & \cdots & G_{2m} \\ \vdots & & \vdots & \vdots & & & \vdots \\ G_{m1} & \cdots & G_{m,s-1} & \Lambda_m & G_{m,s+1} & \cdots & G_{mm} \end{array} \right\},$$

$$+b \sum_{\substack{r=1 \\ r \neq s}}^m \Delta H_r \left\{ \begin{array}{cccccc} G_{11} & \cdots & G_{1,r-1} & \Delta H_1 & G_{1,r+1} & \cdots & G_{1,s-1} & \Lambda_1 & G_{1,s+1} & \cdots & G_{1m} \\ G_{21} & \cdots & G_{2,r-1} & \Delta H_2 & G_{2,r+1} & \cdots & G_{2,s-1} & \Lambda_2 & G_{2,s+1} & \cdots & G_{2m} \\ \vdots & & \vdots & \vdots & & & \vdots & \vdots & & & \vdots \\ G_{m1} & \cdots & G_{m,r-1} & \Delta H_m & G_{m,r+1} & \cdots & G_{m,s-1} & \Lambda_m & G_{m,s+1} & \cdots & G_{mm} \end{array} \right\}. \quad (\text{A.3})$$

The first term on the right-hand side of eq. (A.3) has the same form as the right-hand side of eq. (A.2). Therefore, similarly as in the case of eq. (A.2), we have

$$\sum_{s=1}^m \Delta H_s \left\{ \begin{array}{cccccc} G_{11} & \cdots & G_{1,s-1} & \Lambda_1 & G_{1,s+1} & \cdots & G_{1m} \\ G_{21} & \cdots & G_{2,s-1} & \Lambda_2 & G_{2,s+1} & \cdots & G_{2m} \\ \vdots & & \vdots & \vdots & & & \vdots \\ G_{m1} & \cdots & G_{m,s-1} & \Lambda_m & G_{m,s+1} & \cdots & G_{mm} \end{array} \right\} = \sum_{[i]} \sum_{[j]} \mathbf{R} \left(\begin{array}{c} [i] \\ [j] \end{array} \right) D([i], \Lambda) D([j], \Delta H). \quad (\text{A.4})$$

Substituting eqs. (A.3) and (A.4) back into eq. (25) we see that it only remains to prove that the second term on the right-hand side of eq. (A.3) is equal to zero.

An expression analogous to the second term on the right-hand side of eq. (A.3) was examined in Appendix A of ref. [6], in connection with the proof of formula (31) of ref. [6]; we particularly refer to the last equality in Appendix A. Now, eq. (17) can be rewritten as

$$\mathbf{G} = \mathbf{vRv}^t, \quad (\text{A.5})$$

where $\mathbf{v} = \|\nu_{ij}\|$ is the stoichiometric matrix; notice that eq. (A.5) is the same as eq. (31) in ref. [6]. In view of eq. (A.5), and employing a reasoning described in ref. [6], we conclude that

$$\sum_{r=1}^m \sum_{\substack{s=1 \\ r \neq s}}^m \Delta H_r \Delta H_s \left\{ \begin{array}{cccccc} G_{11} & \cdots & G_{1,r-1} & \Gamma_1 & G_{1,r+1} & \cdots & G_{1,s-1} & \Lambda_1 & G_{1,s+1} & \cdots & G_{1m} \\ G_{21} & \cdots & G_{2,r-1} & \Gamma_2 & G_{2,r+1} & \cdots & G_{2,s-1} & \Lambda_2 & G_{2,s+1} & \cdots & G_{2m} \\ \vdots & & \vdots & \vdots & & & \vdots & \vdots & & & \vdots \\ G_{m1} & \cdots & G_{m,r-1} & \Gamma_m & G_{m,r+1} & \cdots & G_{m,s-1} & \Lambda_m & G_{m,s+1} & \cdots & G_{mm} \end{array} \right\} = \sum_{\{i\}} \sum_{\{j\}} \mathbf{R} \left(\begin{array}{c} \{i\} \\ \{j\} \end{array} \right) D(\{i\}, \Delta H, \Gamma) D(\{j\}, \Delta H, \Lambda), \quad (\text{A.6})$$

where

$$\begin{aligned}
 D(\{i\}, \Delta H, \Gamma) &= \begin{vmatrix} \nu_{1,i_1} & \nu_{1,i_2} & \cdots & \nu_{1,i_{m-2}} & \Delta H_1 & \Gamma_1 \\ \nu_{2,i_1} & \nu_{2,i_2} & \cdots & \nu_{2,i_{m-2}} & \Delta H_2 & \Gamma_2 \\ \vdots & \vdots & & \vdots & \vdots & \vdots \\ \nu_{m,i_1} & \nu_{m,i_m} & \cdots & \nu_{m,i_{m-2}} & \Delta H_m & \Gamma_m \end{vmatrix}, \\
 D(\{j\}, \Delta H, \Lambda) &= \begin{vmatrix} \nu_{1,j_1} & \nu_{1,j_2} & \cdots & \nu_{1,j_{m-2}} & \Delta H_1 & \Lambda_1 \\ \nu_{2,j_1} & \nu_{2,j_2} & \cdots & \nu_{2,j_{m-2}} & \Delta H_2 & \Lambda_2 \\ \vdots & \vdots & & \vdots & \vdots & \vdots \\ \nu_{m,j_1} & \nu_{m,j_m} & \cdots & \nu_{m,j_{m-2}} & \Delta H_m & \Lambda_m \end{vmatrix}.
 \end{aligned}
 \tag{A.7}$$

In the case of eq. (A.3) the parameter Γ_j coincides with ΔH_j , $j = 1, 2, \dots, m$. Therefore the last two columns in the determinant in eq. (A.7) are equal and this determinant vanishes for all $\{i\}$. Then also the right-hand side of eq. (A.6) is equal to zero.

By this we complete the proof of eq. (25).

Proof of eq. (26)

We start with eq. (18). Substituting it into eq. (21) and transforming it in the same way as we did in the case of eq. (A.1), we obtain

$$\mathbf{R} \begin{pmatrix} [i] \\ [j] \end{pmatrix} = \frac{1}{n_i^{m-1}} \left[\mathbf{P} \begin{pmatrix} [i] \\ [j] \end{pmatrix} - a \sum_{k=1}^{m-1} \mathbf{P}_k \begin{pmatrix} [i] \\ [j] \end{pmatrix} \right],
 \tag{A.8}$$

where

$$\mathbf{P}_k \begin{pmatrix} [i] \\ [j] \end{pmatrix} = \begin{vmatrix} P_{i_1 j_1} & \cdots & P_{i_1 j_{k-1}} & 1 & P_{i_1 j_{k+1}} & \cdots & P_{i_1 j_{m-1}} \\ P_{i_2 j_1} & \cdots & P_{i_2 j_{k-1}} & 1 & P_{i_2 j_{k+1}} & \cdots & P_{i_2 j_{m-1}} \\ \vdots & & \vdots & \vdots & \vdots & & \vdots \\ P_{i_{m-1} j_1} & \cdots & P_{i_{m-1} j_{k-1}} & 1 & P_{i_{m-1} j_{k+1}} & \cdots & P_{i_{m-1} j_{m-1}} \end{vmatrix}.$$

Comparing eq. (A.8) with eqs. (25) and (26) we see that what remains to demonstrate is

$$\sum_{[i]} \sum_{[j]} \sum_{k=1}^{m-1} \mathbf{P}_k \begin{pmatrix} [i] \\ [j] \end{pmatrix} D([i], \Lambda) D([j], \Delta H) = \sum_{\{i\}} \sum_{\{j\}} \mathbf{P} \begin{pmatrix} \{i\} \\ \{j\} \end{pmatrix} D(\{i\}, \Lambda) D(\{j\}, \Delta H).
 \tag{A.9}$$

Denote, for brevity, the left-hand side of eq. (A.9) by Q .

By expanding the k th column of the determinant $\mathbf{P}_k \begin{pmatrix} [i] \\ [j] \end{pmatrix}$ in eq. (A.9) we get

$$Q = \sum_{[i]} \sum_{[j]} \sum_{k=1}^{m-1} (-1)^{k+h} \begin{vmatrix} P_{i_1 j_1} & \cdots & P_{i_1 j_{k-1}} & P_{i_1 j_{k+1}} & \cdots & P_{i_1 j_{m-1}} \\ \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\ P_{i_{h-1} j_1} & \cdots & P_{i_{h-1} j_{k-1}} & P_{i_{h-1} j_{k+1}} & \cdots & P_{i_{h-1} j_{m-1}} \\ P_{i_{h+1} j_1} & \cdots & P_{i_{h+1} j_{k-1}} & P_{i_{h+1} j_{k+1}} & \cdots & P_{i_{h+1} j_{m-1}} \\ \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\ P_{i_{m-1} j_1} & \cdots & P_{i_{m-1} j_{k-1}} & P_{i_{m-1} j_{k+1}} & \cdots & P_{i_{m-1} j_{m-1}} \end{vmatrix} \times D([i], \Lambda) D([j], \Delta H). \tag{A.10}$$

Denote now the $(m - 2)$ -tuples $(i_1, i_2, \dots, i_{h-1}, i_{h+1}, \dots, i_{m-1})$ and $(j_1, j_2, \dots, j_{k-1}, j_{k+1}, \dots, j_{m-1})$ by $\{i'\}$ and $\{j'\}$, respectively. With this notation the determinant in eq. (A.10) is equal to $\mathbf{P} \begin{pmatrix} \{i'\} \\ \{j'\} \end{pmatrix}$, see eq. (22). Bearing in mind that [4,6]

$$\sum_{[i]} \sum_{[j]} = \frac{1}{(m - 1)^2} \sum_{\{i'\}} \sum_{\{j'\}} \sum_{i_n=1}^n \sum_{j_k=1}^n$$

it follows that

$$Q = \frac{1}{(m - 1)^2} \sum_{k=1}^{m-1} \sum_{h=1}^{m-1} \sum_{\{i'\}} \sum_{\{j'\}} \sum_{i_h=1}^n \sum_{j_n=1}^n (-1)^{k+h} \mathbf{P} \begin{pmatrix} \{i'\} \\ \{j'\} \end{pmatrix} D([i], \Lambda) D([j], \Delta H).$$

Now, using the definitions (19) and (20), we obtain

$$\begin{aligned} \sum_{i_h=1}^n D([i], \Lambda) &= \begin{vmatrix} \nu_{1,i_1} & \cdots & \nu_{1,i_{h-1}} & \Delta \nu_1 & \nu_{1,i_{h+1}} & \cdots & \nu_{1,i_{m-1}} & \Lambda_1 \\ \nu_{2,i_1} & \cdots & \nu_{2,i_{h-1}} & \Delta \nu_2 & \nu_{2,i_{h+1}} & \cdots & \nu_{2,i_{m-1}} & \Lambda_2 \\ \vdots & & \vdots & \vdots & \vdots & & \vdots & \vdots \\ \nu_{m,i_1} & \cdots & \nu_{m,i_{h-1}} & \Delta \nu_m & \delta m, i_{h+1} & \cdots & \nu_{m,i_{m-1}} & \Lambda_m \end{vmatrix} \\ &= (-1)^{m-1-h} \begin{vmatrix} \nu_{1,i_1} & \cdots & \nu_{1,i_{h-1}} & \nu_{1,i_{h+1}} & \cdots & \nu_{1,i_{m-1}} & \Delta \nu_1 & \Lambda_1 \\ \nu_{2,i_1} & \cdots & \nu_{2,i_{h-1}} & \nu_{2,i_{h+1}} & \cdots & \nu_{2,i_{m-1}} & \Delta \nu_2 & \Lambda_2 \\ \vdots & & \vdots & \vdots & & \vdots & \vdots & \vdots \\ \nu_{m,i_1} & \cdots & \nu_{m,i_{h-1}} & \nu_{m,i_{h+1}} & \cdots & \nu_{m,i_{m-1}} & \Delta \nu_m & \Lambda_m \end{vmatrix} \\ &= (-1)^{m-1-h} D(\{i'\}, \Lambda) \end{aligned}$$

and, similarly,

$$\sum_{jk=1}^n D(\{j\}, \Delta H) = (-1)^{m-1-k} D(\{j'\}, \Delta H).$$

Therefore,

$$\begin{aligned} Q &= \frac{1}{(m-1)^2} \sum_{k=1}^{m-1} \sum_{h=1}^{m-1} \sum_{\{i'\}} \sum_{\{j'\}} (-1)^{k+h+(m-1-k)+(m-1-h)} \mathbf{P} \left(\begin{matrix} \{i'\} \\ \{j'\} \end{matrix} \right) \\ &\quad \times D(\{i'\}, \Lambda) D(\{j'\}, \Delta H) \\ &= \frac{1}{(m-1)^2} \sum_{k=1}^{m-1} \sum_{h=1}^{m-1} \left[\sum_{\{i'\}} \sum_{\{j'\}} \mathbf{P} \left(\begin{matrix} \{i'\} \\ \{j'\} \end{matrix} \right) D(\{i'\}, \Lambda) D(\{j'\}, \Delta H) \right]. \end{aligned} \quad (\text{A.11})$$

Because the expression in square brackets in eq. (A.11) is independent of k and h ,

$$Q = \sum_{\{i'\}} \sum_{\{j'\}} \mathbf{P} \left(\begin{matrix} \{i'\} \\ \{j'\} \end{matrix} \right) D(\{i'\}, \Lambda) D(\{j'\}, \Delta H),$$

which is tantamount to eq. (A.9). The proof of eq. (26) has thus been completed.

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