

Group Additivity Methods in Terms of Response Reactions[†]

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The concept of stoichiometrically unique reactions (response reactions, RERs) is extended to the group additivity (GA) methods. Namely, it is shown that the main assumption of the GA methods according to which chemical species may be “constructed” from a specified number and type of structural units, or groups, may be formally appended to the conventional RER formalism. As a result, one can define and generate a stoichiometrically unique class of GA RERs. Several properties and applications of the newly defined GA RERs are pointed out. In particular, it is proved that the stoichiometry and thermodynamic functions of the GA RERs are interrelated in a simple manner with the error of the GA methods. This finding is used to reformulate the GA methods alternatively (and equivalently), in terms of GA RERs.

1. Introduction

Although much more sophisticated and exact *ab initio* methods¹ are becoming increasingly available, the importance of the classical group additivity (GA) methods^{2–6} is not diminishing. The use of GA methods was shown to be a valuable, effective, and inexpensive technique for the estimation of thermodynamic properties of pure species, even in the era of supercomputers. Moreover, the basic ideas of the GA methods are extensively used to convert the total energies obtained from *ab initio* calculations to conventional thermodynamic functions. It is well-known that the main assumption of the GA methods is that the thermodynamic properties of the chemical species may be partitioned into a sum of contributions associated with a small number of structural units. The thermodynamic properties of the structural units are further assumed to be independent of the nature of the species and may be determined using a representative database of species with known thermodynamic properties. It is often assumed that the GA methods are powerful but limited in scope, in regard to estimation of gas-phase enthalpies of formation of organic compounds, and, perchance, estimation of gas-phase entropies and heat capacities. This assumption is not true: their ability and capability are greater yet. Without meaning to be exhaustive, we mention just a few representative applications from various areas. Thus, GA has been used for decades by the engineering community for the estimation of Lennard-Jones parameters, critical constant estimations, boiling points, etc.⁷ It has even been used for octane ratings.⁸ Some comprehensive applications to the condensed-phase thermochemistry of organic molecules include estimations of enthalpies of formation, heat capacities, absolute entropies and entropies of formation, and phase change entropies and enthalpies: we refer the reader to the extensive studies of Chickos, Domalski, and their respective colleagues.^{9,10} Finally,

the GA methods have been successfully applied to estimate the energetics of free radicals, inorganic and organometallic compounds,¹¹ and aqueous species.¹²

Although both the physicochemical and computational aspects of the GA methods have been exhaustively discussed in the literature, it seems that the stoichiometric aspect of the GA methods has been overlooked. Here, the term “stoichiometric” is used in the following context. As was recognized by Benson,² there exists a hierarchy of additivity schemes. Several levels of approximation exist within this hierarchy. The first level is the atom additivity, followed by the second level (bond additivity), the third level (group additivity), etc. Clearly, the first level is absolutely valid for molecular masses. In fact, the atom additivity is the mathematical expression of the mass balance in the system. As follows from chemical stoichiometry, an alternative (and equivalent) way to express the mass balance in a chemical system is via a set of stoichiometrically independent reactions. The main characteristic of these reactions is the conservation of the number and type of atoms. Generalizing this simple observation, one can alternatively express the GA of chemical species in terms of a set of stoichiometrically independent reactions that, in addition to mass, also preserves the type and number of bonds, groups, etc. Assuming that the GA is absolutely valid (such as mass balance, for instance) would result in chemical reactions that have a remarkable property. Namely, a property change of these reactions should be equal to zero. For instance, if the property of the species is the enthalpy of formation, then a reaction that precisely preserves the type and number of groups would be thermoneutral; i.e., it has an enthalpy change equal to zero.

We have recently addressed the problem of using special classes of stoichiometrically unique chemical reactions, called response reactions (RERs),¹³ to convert accurately the total energies obtained from *ab initio* calculations into enthalpies of formation of the species.¹⁴ The purpose of the present work is to extend the RERs approach to the GA methods. More specifically, we show that the group-preserving conditions may

[†] Dedicated to Prof. Benson on the occasion of his 85th birthday.

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be easily incorporated into the RERs formalism. As a result, one can visualize, generate, and enumerate a special class of stoichiometrically unique GA reactions, e.g., GA RERs. Because of their stoichiometric uniqueness, we further show that the GA methods may be reformulated in terms of RERs. In particular, the properties of the species may be evaluated without explicitly determining the values of the group contributions.

2. Notation and Definitions

We consider a general multiple chemical reaction system comprising a set of n species A_1, A_2, \dots, A_n . Each of the species in this system is characterized by a certain *composition* and *structure*. Here, the term “composition” means a specified number s of elements B_1, B_2, \dots, B_s , e.g., any set of stoichiometrically appropriate atomic, molecular, or ionic entities that may be used to “construct” the species A_i :

$$A_i = \sum_{l=1}^s \beta_{il} B_l \quad (1)$$

Here, β_{il} ($i = 1, 2, \dots, n; l = 1, 2, \dots, s$) is the number of elements B_l in species A_i . The matrix β ,

$$\beta = \begin{bmatrix} \beta_{11} & \beta_{12} & \dots & \beta_{1s} \\ \beta_{21} & \beta_{22} & \dots & \beta_{2s} \\ \dots & \dots & \dots & \dots \\ \beta_{n1} & \beta_{n2} & \dots & \beta_{ns} \end{bmatrix} \quad (2)$$

is normally called the formula matrix.¹⁵ For simplicity, we assume that the rank of the formula matrix is equal to the number of elements s , i.e., $\text{rank } \beta = s$.

The term “structure” of the species means a specified type g_j ($j = 1, 2, \dots, p$) and number g_{ij} ($i = 1, 2, \dots, n; j = 1, 2, \dots, p$) of groups in a chemical species A_i ($i = 1, 2, \dots, n$). Here, the term “group” is used in exactly the same sense as in the conventional GA methods; that is, “a polyvalent atom (ligancy ≥ 2) in a molecule together with all of its ligands”.³ Thus, we can define the matrix g' , which may be called the group matrix.

$$g' = \begin{bmatrix} g_{11} & g_{12} & \dots & g_{1p} \\ g_{21} & g_{22} & \dots & g_{2p} \\ \dots & \dots & \dots & \dots \\ g_{n1} & g_{n2} & \dots & g_{np} \end{bmatrix}$$

For simplicity, in this work, we consider only one property, namely, the ideal gas-phase standard enthalpy of formation of the species A_i ($i = 1, 2, \dots, n$), conventionally denoted by $\Delta_f H_{298}^\circ(A_i)$. If $\Delta_f H_{298}^\circ(g_j)$ is the group value of g_j ($j = 1, 2, \dots, p$), then we have

$$\begin{aligned} \Delta_f H_{298}^\circ(A_1) &= g_{11} \Delta_f H_{298}^\circ(g_1) + \\ &\quad g_{12} \Delta_f H_{298}^\circ(g_2) + \dots + g_{1p} \Delta_f H_{298}^\circ(g_p) \\ \Delta_f H_{298}^\circ(A_2) &= g_{21} \Delta_f H_{298}^\circ(g_1) + \\ &\quad g_{22} \Delta_f H_{298}^\circ(g_2) + \dots + g_{2p} \Delta_f H_{298}^\circ(g_p) \\ &\vdots \\ \Delta_f H_{298}^\circ(A_n) &= g_{n1} \Delta_f H_{298}^\circ(g_1) + \\ &\quad g_{n2} \Delta_f H_{298}^\circ(g_2) + \dots + g_{np} \Delta_f H_{298}^\circ(g_p) \end{aligned} \quad (3)$$

or, in a more concise matrix form,

$$\begin{pmatrix} \Delta_f H_{298}^\circ(A_1) \\ \Delta_f H_{298}^\circ(A_2) \\ \dots \\ \Delta_f H_{298}^\circ(A_n) \end{pmatrix} = \begin{bmatrix} g_{11} & g_{12} & \dots & g_{1p} \\ g_{21} & g_{22} & \dots & g_{2p} \\ \dots & \dots & \dots & \dots \\ g_{n1} & g_{n2} & \dots & g_{np} \end{bmatrix} \begin{pmatrix} \Delta_f H_{298}^\circ(g_1) \\ \Delta_f H_{298}^\circ(g_2) \\ \dots \\ \Delta_f H_{298}^\circ(g_p) \end{pmatrix}$$

The formula and group matrices may be further combined into one formula-group matrix:

$$\Gamma' = \begin{bmatrix} \beta_{11} & \beta_{12} & \dots & \beta_{1s} & g_{11} & g_{12} & \dots & g_{1p} \\ \beta_{21} & \beta_{22} & \dots & \beta_{2s} & g_{21} & g_{22} & \dots & g_{2p} \\ \dots & \dots & \dots & \dots & \dots & \dots & \dots & \dots \\ \beta_{n1} & \beta_{n2} & \dots & \beta_{ns} & g_{n1} & g_{n2} & \dots & g_{np} \end{bmatrix} \quad (4)$$

The formula-group matrix is a quantitative characteristic of both the composition and the structure of a chemical system. Normally, the columns in this matrix are linearly dependent; that is, $\text{rank } \Gamma' = q < s + p$. For our purposes, however, we need to consider only an arbitrarily chosen subset of linearly independent columns from the formula-group matrix. We choose them by performing a column reduction operation on the formula-bond matrix, such that

$$\sum_{j=1}^s a_{jh} \begin{bmatrix} \beta_{1j} \\ \beta_{2j} \\ \dots \\ \beta_{nj} \end{bmatrix} + \sum_{k=1}^p b_{kh} \begin{bmatrix} g_{1k} \\ g_{2k} \\ \dots \\ g_{nk} \end{bmatrix} = \begin{bmatrix} \Gamma_{1h} \\ \Gamma_{2h} \\ \dots \\ \Gamma_{nh} \end{bmatrix} \quad (h = 1, 2, \dots, q) \quad (5)$$

$$\sum_{j=1}^s a_{jh} \begin{bmatrix} \beta_{1j} \\ \beta_{2j} \\ \dots \\ \beta_{nj} \end{bmatrix} + \sum_{k=1}^p b_{kh} \begin{bmatrix} g_{1k} \\ g_{2k} \\ \dots \\ g_{nk} \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \\ \dots \\ 0 \end{bmatrix} \quad (h = q + 1, q + 2, \dots, s + p) \quad (6)$$

where a_{jh} and b_{kh} are constants. Thus, we can define a *reduced* formula-bond matrix,

$$\Gamma = \begin{bmatrix} \Gamma_{11} & \Gamma_{12} & \dots & \Gamma_{1q} \\ \Gamma_{21} & \Gamma_{22} & \dots & \Gamma_{2q} \\ \dots & \dots & \dots & \dots \\ \Gamma_{n1} & \Gamma_{n2} & \dots & \Gamma_{nq} \end{bmatrix} \quad (7)$$

in which the columns are linearly independent and, consequently, $\text{rank } \Gamma = q$.

Consider further a general chemical reaction r :

$$r = \nu_1 B_1 + \nu_2 B_2 + \dots + \nu_n B_n = 0 \quad (8)$$

where ν_i ($i = 1, 2, \dots, n$) are the stoichiometric coefficients assumed as usual to take positive values for products and negative for reactants. Obviously, every chemical reaction satisfies the mass-balance conditions

$$\begin{aligned} \nu_1 \beta_{11} + \nu_2 \beta_{21} + \dots + \nu_n \beta_{n1} &= 0 \\ \nu_1 \beta_{12} + \nu_2 \beta_{22} + \dots + \nu_n \beta_{n2} &= 0 \\ &\vdots \\ \nu_1 \beta_{1s} + \nu_2 \beta_{2s} + \dots + \nu_n \beta_{ns} &= 0 \end{aligned} \quad (9)$$

It is well-known¹⁵ that, in the absence of any other additional stoichiometric constraints, the number of linearly independent reactions m is equal to $m = n - \text{rank } \beta = n - s$.

A reaction that concomitantly satisfies the group-preserving conditions

$$\begin{aligned} \nu_1 g_{11} + \nu_2 g_{21} + \dots + \nu_n g_{n1} &= 0 \\ \nu_1 g_{12} + \nu_2 g_{22} + \dots + \nu_n g_{n2} &= 0 \\ &\vdots \\ \nu_1 g_{1p} + \nu_2 g_{2p} + \dots + \nu_n g_{np} &= 0 \end{aligned} \quad (10)$$

is called a GA reaction. Given eqs 5 and 6, a GA reaction may be alternatively defined as one that satisfies the condition

$$\begin{aligned} \nu_1 \Gamma_{11} + \nu_2 \Gamma_{21} + \dots + \nu_n \Gamma_{n1} &= 0 \\ \nu_1 \Gamma_{12} + \nu_2 \Gamma_{22} + \dots + \nu_n \Gamma_{n2} &= 0 \\ &\vdots \\ \nu_1 \Gamma_{1q} + \nu_2 \Gamma_{2q} + \dots + \nu_n \Gamma_{nq} &= 0 \end{aligned} \quad (11)$$

We mention also that the number of linearly independent GA reactions is equal to $m = n - \text{rank } \Gamma = n - q$. A set of linearly independent GA reactions may be derived by solving eq 11, using any appropriate linear algebra procedure and numerical analysis.

3. GA RERs

The RERs formalism discussed in detail in our previous publications may be easily generalized. Thus, by analogy with conventional¹³ and isodesmic¹⁴ RERs, we can define a new type of RER.

Definition: A reaction that is additionally subject to group-preserving conditions and involves no more than (rank $\Gamma + 1$) = $q + 1$ species is called a GA RER.

Let $A_{i_1}, A_{i_2}, \dots, A_{i_q}, A_{i_{q+1}}$ ($1 \leq i_1 < i_2 < \dots < i_q < i_{q+1} \leq n$) be the $q + 1$ species involved in a GA RER. Such a RER is denoted by $g(A_{i_1}, A_{i_2}, \dots, A_{i_q}, A_{i_{q+1}})$, and its general equation is given as

$$g(A_{i_1}, A_{i_2}, \dots, A_{i_q}, A_{i_{q+1}}) = \begin{vmatrix} \Gamma_{i_1,1} & \Gamma_{i_1,2} & \dots & \Gamma_{i_1,q} & B_{i_1} \\ \Gamma_{i_2,1} & \Gamma_{i_2,2} & \dots & \Gamma_{i_2,q} & B_{i_2} \\ \dots & \dots & \dots & \dots & \dots \\ \Gamma_{i_q,1} & \Gamma_{i_q,2} & \dots & \Gamma_{i_q,q} & B_{i_q} \\ \Gamma_{i_{q+1},1} & \Gamma_{i_{q+1},2} & \dots & \Gamma_{i_{q+1},q} & B_{i_{q+1}} \end{vmatrix} = 0 \quad (12)$$

A complete set of GA RERs may be generated by considering all the possible choices of $q + 1$ species from a total of n . In other words, the total number N of GA RERs does not exceed

$$N = \frac{n!}{(q+1)!(n-q-1)!}$$

It is to be noted that not necessarily all the GA RERs are stoichiometrically distinct. That is, some of the stoichiometric coefficients in a GA RER (or, even all) may be equal to zero, thus resulting in stoichiometrically equivalent isostoichiometric RERs. Even so, the number of stoichiometrically distinct GA RERs exceeds the number of linearly independent ones.

The enthalpy changes of the GA RERs denoted as $\Delta H(g) = \Delta H(A_{i_1}, A_{i_2}, \dots, A_{i_q}, A_{i_{q+1}})$ are interrelated with the standard enthalpies of formation $\Delta_f H_{298}^\circ(A_{ik})$ of the species via

$$\Delta H(g) = \Delta H(A_{i_1}, A_{i_2}, \dots, A_{i_q}, A_{i_{q+1}}) = \begin{vmatrix} \Gamma_{i_1,1} & \Gamma_{i_1,2} & \dots & \Gamma_{i_1,q} & \Delta_f H_{298}^\circ(A_{i_1}) \\ \Gamma_{i_2,1} & \Gamma_{i_2,2} & \dots & \Gamma_{i_2,q} & \Delta_f H_{298}^\circ(A_{i_2}) \\ \dots & \dots & \dots & \dots & \dots \\ \Gamma_{i_q,1} & \Gamma_{i_q,2} & \dots & \Gamma_{i_q,q} & \Delta_f H_{298}^\circ(A_{i_q}) \\ \Gamma_{i_{q+1},1} & \Gamma_{i_{q+1},2} & \dots & \Gamma_{i_{q+1},q} & \Delta_f H_{298}^\circ(A_{i_{q+1}}) \end{vmatrix} \quad (13)$$

4. Group Additivity, in Terms of Group Additivity Response Reactions

We are now in a position to formulate the following property of GA RERs: *provided the GA is strictly valid, the enthalpy changes of GA RERs are equal to zero, i.e.,*

$$\Delta H(g) = \Delta H(A_{i_1}, A_{i_2}, \dots, A_{i_q}, A_{i_{q+1}}) = 0 \quad (14)$$

The proof of this statement is given in the Appendix.

This property of the GA RERs may be used to reformulate the GA methods in terms of GA RERs. The reasoning is as follows. Consider the evaluation of the standard enthalpy of formation of a given species, say A_1 , assuming that the standard enthalpy of formation of the remaining species A_2, A_3, \dots, A_n is known. First, we enumerate a complete set of GA RERs involving species A_1 . Because the number of species involved in a GA RER does not exceed $q + 1$ species, to enumerate a complete set of GA RERs involving species A_1 , we need to specify only q species from the remaining $n - 1$. If these q species are $A_{i_1}, A_{i_2}, \dots, A_{i_q}$ ($2 \leq i_1 < i_2 < \dots < i_q < n$), then, according to the above-described development, the general equation of a GA RER involving species A_1 is given by

$$g(A_1, A_{i_1}, A_{i_2}, \dots, A_{i_q}) = \begin{vmatrix} \Gamma_{11} & \Gamma_{12} & \dots & \Gamma_{1q} & A_1 \\ \Gamma_{i_1,1} & \Gamma_{i_1,2} & \dots & \Gamma_{i_1,q} & A_{i_1} \\ \Gamma_{i_2,1} & \Gamma_{i_2,2} & \dots & \Gamma_{i_2,q} & A_{i_2} \\ \dots & \dots & \dots & \dots & \dots \\ \Gamma_{i_q,1} & \Gamma_{i_q,2} & \dots & \Gamma_{i_q,q} & A_{i_q} \end{vmatrix} = 0 \quad (15)$$

Thus, the total number of GA RERs involving B_1 does not exceed

$$N = \frac{(n-1)!}{q!(n-q-1)!}$$

Now, assuming that the GA method is exact (that is, the enthalpy change of every GA RER is equal to zero), the standard enthalpy of formation of species A_1 may be evaluated by solving the following equation for $\Delta_f H_{298}^\circ(A_1)_{\text{calc}}$:

$$\begin{vmatrix} \Gamma_{11} & \Gamma_{12} & \dots & \Gamma_{1q} & \Delta_f H_{298}^\circ(A_1)_{\text{calc}} \\ \Gamma_{i_1,1} & \Gamma_{i_1,2} & \dots & \Gamma_{i_1,q} & \Delta_f H_{298}^\circ(A_{i_1})_{\text{exp}} \\ \Gamma_{i_2,1} & \Gamma_{i_2,2} & \dots & \Gamma_{i_2,q} & \Delta_f H_{298}^\circ(A_{i_2})_{\text{exp}} \\ \dots & \dots & \dots & \dots & \dots \\ \Gamma_{i_q,1} & \Gamma_{i_q,2} & \dots & \Gamma_{i_q,q} & \Delta_f H_{298}^\circ(A_{i_q})_{\text{exp}} \end{vmatrix} = 0 \quad (16)$$

In reality, the enthalpy change for every GA RER is not strictly equal to zero, because the GA methods are approximate:

$$\Delta H(g) = \begin{vmatrix} \Gamma_{11} & \Gamma_{12} & \dots & \Gamma_{1q} & \Delta_f H_{298}^\circ(A_1)_{\text{exp}} \\ \Gamma_{i_1,1} & \Gamma_{i_1,2} & \dots & \Gamma_{i_1,q} & \Delta_f H_{298}^\circ(A_{i_1})_{\text{exp}} \\ \Gamma_{i_2,1} & \Gamma_{i_2,2} & \dots & \Gamma_{i_2,q} & \Delta_f H_{298}^\circ(A_{i_2})_{\text{exp}} \\ \dots & \dots & \dots & \dots & \dots \\ \Gamma_{i_q,1} & \Gamma_{i_q,2} & \dots & \Gamma_{i_q,q} & \Delta_f H_{298}^\circ(A_{i_q})_{\text{exp}} \end{vmatrix} \neq 0 \quad (17)$$

Comparing eqs 16 and 17, we find that

$$\Delta_f H_{298}^\circ(A_1)_{\text{exp}} - \Delta_f H_{298}^\circ(A_1)_{\text{calc}} = \frac{1}{\delta(g)} \Delta H(g) \quad (18)$$

where $\delta(g)$ is the stoichiometric coefficient of species A_1 in the GA RER $g(A_1, A_{i_1}, A_{i_2}, \dots, A_{i_q})$ and is given by

$$\delta(g) = \begin{vmatrix} \Gamma_{11} & \Gamma_{12} & \dots & \Gamma_{1q} & 1 \\ \Gamma_{i_1,1} & \Gamma_{i_1,2} & \dots & \Gamma_{i_1,q} & 0 \\ \Gamma_{i_2,1} & \Gamma_{i_2,2} & \dots & \Gamma_{i_2,q} & 0 \\ \dots & \dots & \dots & \dots & \dots \\ \Gamma_{i_q,1} & \Gamma_{i_q,2} & \dots & \Gamma_{i_q,q} & 0 \end{vmatrix}$$

As can be seen from eq 18, the enthalpy change of a GA RER ($\Delta H(g)$) is nothing but a measure of the error of the GA methods.

Solving eq 16 for every GA RER and taking the average results in the final value of the standard enthalpy of formation $\Delta_f H_{298}^\circ(A_1)_{\text{calc}}$ of species A_1 . Notice that, within the GA RER approach, there is no need to introduce the GA values.

5. Examples

The above-described theoretical considerations are next illustrated with the help of two examples. It should be noticed that it is not our intention to compare the numerical output of the GA RER approach with the conventional GA methods. A thorough comparison of these approaches will be presented elsewhere. Rather, the examples are mainly intended to illustrate the technique of the GA RER approach.

5.1. Example 1. Consider the following hydrocarbons: A_1 , 2-methylpropane (−32.07 kcal/mol); A_2 , 2-methylbutane (−36.74 kcal/mol); A_3 , 2-methylpentane (−41.78 kcal/mol); A_4 , 3-methylpentane (−41.13 kcal/mol); A_5 , 2-methylhexane (−46.51 kcal/mol); and A_6 , 3-methylhexane (−45.72 kcal/mol). The values given in parentheses are the experimental standard enthalpies of formation of the respective hydrocarbons, without considering only the most stable conformer.³ For illustration purposes, we consider here the Benson's group classification,³ according to which saturated hydrocarbons are assumed to contain primary (g_1), secondary (g_2), tertiary (g_3), and quaternary (g_4) C atoms. Benson's classification also postulates two additional types of nonbonded atom interactions, namely, 1–4 (g_5) and 1–5 (g_6) interactions. Thus, the formula-group matrix for this system is

$$\mathbf{\Gamma} = \begin{vmatrix} \text{C} & \text{H} & g_1 & g_2 & g_3 & g_4 & g_5 & g_6 \\ 4 & 10 & 3 & 0 & 1 & 0 & 0 & 0 \\ 5 & 12 & 3 & 1 & 1 & 0 & 0 & 0 \\ 6 & 14 & 3 & 2 & 1 & 0 & 1 & 0 \\ 6 & 14 & 3 & 2 & 1 & 0 & 2 & 0 \\ 7 & 16 & 3 & 3 & 1 & 0 & 1 & 0 \\ 7 & 16 & 3 & 3 & 1 & 0 & 2 & 0 \end{vmatrix} \begin{matrix} A_1 \\ A_2 \\ A_3 \\ A_4 \\ A_5 \\ A_6 \end{matrix}$$

Using the RowReduce[$\mathbf{\Gamma}$]/MatrixForm command in *Math-*

ematica,¹⁶ this matrix may be readily transformed to

$$\mathbf{\Gamma}' = \begin{bmatrix} 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ 1 & -2 & 2 & 0 & 0 & 0 & 0 & 0 \\ -1 & 1 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & -1 & 2 & 0 & 0 & 0 & 0 & 0 \end{bmatrix} \begin{matrix} A_1 \\ A_2 \\ A_3 \\ A_4 \\ A_5 \\ A_6 \end{matrix}$$

It is seen that rank $\mathbf{\Gamma}' = 3$; hence, an appropriate reduced formula-bond matrix is

$$\mathbf{\Gamma} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & -2 & 2 \\ -1 & 1 & 1 \\ 0 & -1 & 2 \end{bmatrix} \begin{matrix} A_1 \\ A_2 \\ A_3 \\ A_4 \\ A_5 \\ A_6 \end{matrix}$$

Now, by definition, a GA RER involves no more than four species ((rank $\mathbf{\Gamma}$) + 1 = 3 + 1 = 4) in this example; consequently, the total number of GA RERs will not exceed (6!/2!)/4! = 15. For instance, the species A_1 , A_4 , A_5 , and A_6 define the following GA RER:

$$g(A_1, A_4, A_5, A_6) = \begin{vmatrix} 1 & 0 & 0 & A_1 \\ 1 & -2 & 2 & A_4 \\ -1 & 1 & 1 & A_5 \\ 0 & -1 & 2 & A_6 \end{vmatrix} \\ = -A_1 + 3A_4 + 2A_5 - 4A_6 = 0$$

The enthalpy change of this GA RER is equal to

$$\Delta H(g) = \Delta H(A_1, A_4, A_5, A_6) = \begin{vmatrix} 1 & 0 & 0 & \Delta_f H_{298}^\circ(A_1) \\ 1 & -2 & 2 & \Delta_f H_{298}^\circ(A_4) \\ -1 & 1 & 1 & \Delta_f H_{298}^\circ(A_5) \\ 0 & -1 & 2 & \Delta_f H_{298}^\circ(A_6) \end{vmatrix} \\ = -\Delta_f H_{298}^\circ(A_1) + 3\Delta_f H_{298}^\circ(A_4) + 2\Delta_f H_{298}^\circ(A_5) - 4\Delta_f H_{298}^\circ(A_6) = -1.46 \text{ kcal/mol}$$

It is seen that, although the enthalpy change of this GA RER is quite small, it is not, however, equal to zero, reflecting, thus, the simple fact that the GA is approximate. To estimate the standard enthalpy changes of a certain species, say A_4 , from the above-described GA RER, we assume that the enthalpy change of this GA RER is precisely equal to zero and solve the following equation for $x = \Delta_f H_{298}^\circ(A_4)_{\text{calc}}$:

$$\begin{vmatrix} 1 & 0 & 0 & \Delta_f H_{298}^\circ(A_1) \\ 1 & -2 & 2 & x \\ -1 & 1 & 1 & \Delta_f H_{298}^\circ(A_5) \\ 0 & -1 & 2 & \Delta_f H_{298}^\circ(A_6) \end{vmatrix} = 0$$

The solution of this equation is $x = \Delta_f H_{298}^\circ(A_4)_{\text{calc}} = -40.64$ kcal/mol. This value should be compared with the experimental value, $\Delta_f H_{298}^\circ(A_4)_{\text{exp}} = -41.13$ kcal/mol. Alternatively, we can use eq 18 to determine the difference between the experimental and calculated values of the standard enthalpy of formation directly:

$$\Delta_f H_{298}^\circ(A_4)_{\text{exp}} - \Delta_f H_{298}^\circ(A_4)_{\text{calc}} = -\frac{1.46}{3} = -0.49 \text{ kcal/mol}$$

TABLE 1: Complete Set of GA RERs, Enthalpy Changes, and Estimated Errors in the Enthalpy of Formation of the Species Considered in Example 1

GA RERs	ΔH_f°	$\Delta_f H_{298}^\circ(A_i)_{\text{exp}} - \Delta_f H_{298}^\circ(A_i)_{\text{calc}}$					
		B ₁	B ₂	B ₃	B ₄	B ₅	B ₆
1. $-B_1 + 2B_2 - 2B_3 + B_4 = 0$	-1.02	1.02	-0.51	0.51	-1.02		
2. $B_1 - B_2 - B_3 + B_5 = 0$	-0.06	-0.06	0.06	0.06		-0.06	
3. $3B_1 - 4B_2 - B_4 + 2B_5 = 0$	-1.14	-0.38	0.29		1.14	-0.57	
4. $B_1 - B_2 - B_4 + B_6 = 0$	0.08	0.08	-0.08		-0.08		0.08
5. $-2B_1 + 3B_2 - 2B_5 + B_6 = 0$	1.22	-0.61	0.41			-0.61	1.22
6. $B_1 - 4B_3 + B_4 + 2B_5 = 0$	0.90	0.90		-0.23	0.90	0.45	
7. $B_1 - 2B_3 - B_4 + 2B_6 = 0$	1.18	1.18		-0.59	1.04		0.59
8. $-B_1 + 3B_3 - B_5 - B_6 = 0$	-1.04	-1.04		-0.35		1.04	1.04
9. $-B_1 + 3B_4 + 2B_5 - 4B_6 = 0$	-1.46	1.46			-0.49	-0.73	0.37
10. $B_2 - 3B_3 + B_4 + B_5 = 0$	0.96		0.96	-0.32	0.95	0.96	
11. $B_2 - 2B_3 + B_6 = 0$	1.10		1.10	-0.55			1.10
12. $-B_2 + 2B_4 + 2B_5 - 3B_6 = 0$	-1.38		1.38		-0.69	-0.69	0.46
13. $-B_3 + B_4 + B_5 - B_6 = 0$	-0.14			0.14	-0.14	-0.14	0.14
	av	0.51	0.45	-0.17	0.15	-0.04	0.62

For a given species, this procedure should be done over a complete set of GA RERs. The results of such an analysis for all six species are summarized in Table 1. Notice that, from a total of 15 possible GA RERs, only 13 are stoichiometrically distinct.

5.2. Example 2. As a second example, consider the class of chlorinated methanes: CH₄ (-17.8 kcal/mol), CH₃Cl (-20.0 kcal/mol), CH₂Cl₂ (-22.8 kcal/mol), CHCl₃ (-24.6 kcal/mol), and CCl₄ (-22.9 kcal/mol), where the values given in parentheses represent the experimental standard enthalpies of formation of the respective species. For illustration purposes, we consider here two different classifications of the groups that are referenced further as the first and second approximations and are similar to those proposed by Bozzelli and co-workers.¹⁷

First Approximation. First, consider the following three types of contributions to the enthalpy: $g_1 = \text{H-C-H}$, $g_2 = \text{H-C-Cl}$, and $g_3 = \text{Cl-C-Cl}$. Alternatively, this classification may be treated as pair interaction among H and Cl atoms: $g_1, \text{H...H}$; $g_2, \text{H...Cl}$; and $g_3, \text{Cl...Cl}$. The following formula-group matrix may be readily generated on the basis of this classification:

$$\mathbf{\Gamma} = \begin{matrix} & \text{C} & \text{H} & \text{Cl} & g_1 & g_2 & g_3 \\ \begin{bmatrix} 1 & 4 & 0 & 6 & 0 & 0 \\ 1 & 3 & 1 & 3 & 3 & 3 \\ 1 & 2 & 2 & 1 & 4 & 1 \\ 1 & 1 & 3 & 0 & 3 & 3 \\ 1 & 0 & 4 & 0 & 0 & 6 \end{bmatrix} & \text{CH}_4 \\ & \text{CH}_3\text{Cl} \\ & \text{CH}_2\text{Cl}_2 \\ & \text{CHCl}_3 \\ & \text{CCl}_4 \end{matrix}$$

Using Mathematica with the RowReduce[$\mathbf{\Gamma}$]/MatrixForm command, we obtain

$$\mathbf{\Gamma}' = \begin{bmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 1 & -3 & 3 & 0 & 0 & 0 \\ 3 & -8 & 6 & 0 & 0 & 0 \end{bmatrix} \begin{matrix} \text{CH}_4 \\ \text{CH}_3\text{Cl} \\ \text{CH}_2\text{Cl}_2 \\ \text{CHCl}_3 \\ \text{CCl}_4 \end{matrix}$$

Thus, rank $\mathbf{\Gamma}' = 3$ and an appropriate reduced formula-group matrix is

$$\mathbf{\Gamma} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & -3 & 3 \\ 3 & -8 & 6 \end{bmatrix} \begin{matrix} \text{CH}_4 \\ \text{CH}_3\text{Cl} \\ \text{CH}_2\text{Cl}_2 \\ \text{CHCl}_3 \\ \text{CCl}_4 \end{matrix}$$

By definition, a GA RER involves no more than four species ((rank $\mathbf{\Gamma}'$) + 1 = 3 + 1 = 4) in this example. Consequently, the number of GA RERs does not exceed the number of ways four species may be selected from a total of five, i.e., (5!/4!)/1! = 5. For instance, the first four species define the following GA RER:

$$g(\text{CH}_4, \text{CH}_3\text{Cl}, \text{CH}_2\text{Cl}_2, \text{CHCl}_3) = \begin{vmatrix} 1 & 0 & 0 & \text{CH}_4 \\ 0 & 1 & 0 & \text{CH}_3\text{Cl} \\ 0 & 0 & 1 & \text{CH}_2\text{Cl}_2 \\ 1 & -3 & 3 & \text{CHCl}_3 \end{vmatrix} \\ = -\text{CH}_4 - 3\text{CH}_2\text{Cl}_2 + 3\text{CH}_3\text{Cl} + \text{CHCl}_3 = 0$$

The enthalpy change of this GA RER is

$$\Delta H(g) = \Delta H(\text{CH}_4, \text{CH}_3\text{Cl}, \text{CH}_2\text{Cl}_2, \text{CHCl}_3) \\ = \begin{vmatrix} 1 & 0 & 0 & -17.8 \\ 0 & 1 & 0 & -20.0 \\ 0 & 0 & 1 & -22.8 \\ 1 & -3 & 3 & -24.7 \end{vmatrix} = 1.6 \text{ kcal/mol}$$

This enthalpy change is directly related to the error of the GA methods in the estimation of the enthalpy change of the species. Thus, according to eq 18, the GA RER $g(\text{CH}_4, \text{CH}_3\text{Cl}, \text{CH}_2\text{Cl}_2, \text{CHCl}_3)$ values predict the following errors in the enthalpies of formation of the species involved in this GA RER:

$$\Delta_f H_{298}^\circ(\text{CH}_4)_{\text{exp}} - \Delta_f H_{298}^\circ(\text{CH}_4)_{\text{calc}} = -\frac{1.6}{1} \\ = -1.6 \text{ kcal/mol}$$

$$\Delta_f H_{298}^\circ(\text{CH}_3\text{Cl})_{\text{exp}} - \Delta_f H_{298}^\circ(\text{CH}_3\text{Cl})_{\text{calc}} = \frac{1.6}{3} \\ = 0.5 \text{ kcal/mol}$$

$$\Delta_f H_{298}^\circ(\text{CH}_2\text{Cl}_2)_{\text{exp}} - \Delta_f H_{298}^\circ(\text{CH}_2\text{Cl}_2)_{\text{calc}} = -\frac{1.6}{3} \\ = -0.5 \text{ kcal/mol}$$

$$\Delta_f H_{298}^\circ(\text{CHCl}_3)_{\text{exp}} - \Delta_f H_{298}^\circ(\text{CHCl}_3)_{\text{calc}} = \frac{1.6}{1} \\ = 1.6 \text{ kcal/mol}$$

A complete list of GA RERs, along with the average errors in

TABLE 2: Complete Set of GA RERs, Enthalpy Changes, and Estimated Errors in the Enthalpy of Formation of the Species Considered in Example 2

GA RER	ΔH_j°	$\Delta_f H_{298}^\circ - \Delta_f H_{298}^\circ(A_i)_{\text{calc}}$				
		CH ₄	CH ₃ Cl	CH ₂ Cl ₂	CHCl ₃	CCl ₄
	first approximation					
1. $-\text{CH}_4 - 3\text{CH}_2\text{Cl}_2 + \text{CHCl}_3 + 3\text{CH}_3\text{Cl} = 0$	1.6	-1.6	0.5	-0.5	1.6	
2. $-3\text{CH}_4 - 6\text{CH}_2\text{Cl}_2 + \text{CCl}_4 + 8\text{CH}_3\text{Cl} = 0$	7.3	-2.4	0.9	-1.2		7.3
3. $-\text{CH}_4 - 2\text{CHCl}_3 + \text{CCl}_4 + 2\text{CH}_3\text{Cl} = 0$	4.1	-4.1	2.1		-2.1	4.1
4. $-\text{CH}_4 - 8\text{CHCl}_3 + 3\text{CCl}_4 + 6\text{CH}_2\text{Cl}_2 = 0$	9.1	-9.1		1.5	-1.1	3.0
5. $-\text{CH}_3\text{Cl} - 3\text{CHCl}_3 + \text{CCl}_4 + 3\text{CH}_2\text{Cl}_2 = 0$	2.5		-2.5	0.8	-0.8	2.5
	av	-4.3	0.25	0.15	-0.6	4.2
	second approximation					
$-\text{CH}_4 - \text{CCl}_4 - 6\text{CH}_2\text{Cl}_2 + 4\text{CH}_3\text{Cl} + 4\text{CHCl}_3 = 0$	-0.9	0.9	0.25	0.15	-0.25	0.9

the estimation of the enthalpies of formation of species, is presented in Table 2. It is seen that the adopted classification of groups works well for the intermediate chlorinated methanes but is poor for CH₄ and CCl₄.

Second Approximation. The accuracy of GA methods may be increased upon acceptance of a more detailed classification of the groups. Thus, we may replace the pair interaction of atoms by a tri-atom interaction. As chronicled by Cox and Pilcher¹⁸ in their now-classic volume on thermochemistry, tri-atom additivity methods are decades old, commencing with early work by Zahn nearly 70 years ago¹⁹ and evolving through numerous extensions and amplifications. Although tri-atom additivity is generally of higher accuracy than group additivity, it is considerably more complicated and the desired input parameters and data are often absent. This classification results in four contributions to the enthalpy: g_4 , CH₃; g_5 , CH₂-Cl; g_6 , CHCl₂; and g_7 , CCl₃. The formula-group matrix in this case is

$$\mathbf{\Gamma}' = \begin{bmatrix} \text{C} & \text{H} & \text{Cl} & g_4 & g_5 & g_6 & g_7 \\ 1 & 4 & 0 & 4 & 0 & 0 & 0 \\ 1 & 3 & 1 & 1 & 3 & 0 & 0 \\ 1 & 2 & 2 & 0 & 2 & 2 & 0 \\ 1 & 1 & 3 & 0 & 0 & 3 & 1 \\ 1 & 0 & 4 & 0 & 0 & 0 & 4 \end{bmatrix} \begin{matrix} \text{CH}_4 \\ \text{CH}_3\text{Cl} \\ \text{CH}_2\text{Cl}_2 \\ \text{CHCl}_3 \\ \text{CCl}_4 \end{matrix}$$

After reduction, the formula-group matrix takes the form

$$\mathbf{\Gamma}' = \begin{bmatrix} 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ -1 & 4 & -6 & 4 & 0 & 0 & 0 \end{bmatrix} \begin{matrix} \text{CH}_4 \\ \text{CH}_3\text{Cl} \\ \text{CH}_2\text{Cl}_2 \\ \text{CHCl}_3 \\ \text{CCl}_4 \end{matrix}$$

Hence, rank $\mathbf{\Gamma}' = 4$ and the reduced formula-group matrix is

$$\mathbf{\Gamma} = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ -1 & 4 & -6 & 4 \end{bmatrix} \begin{matrix} \text{CH}_4 \\ \text{CH}_3\text{Cl} \\ \text{CH}_2\text{Cl}_2 \\ \text{CHCl}_3 \\ \text{CCl}_4 \end{matrix}$$

Because a GA RER involves no more than five species ((rank $\mathbf{\Gamma}'$) + 1 = 4 + 1 = 5) in this example, we conclude that, under

this classification, there is only one GA RER that is given by

$$g(\text{CH}_4, \text{CH}_3\text{Cl}, \text{CH}_2\text{Cl}_2, \text{CHCl}_3, \text{CCl}_4) = \begin{bmatrix} 1 & 0 & 0 & 0 & \text{CH}_4 \\ 0 & 1 & 0 & 0 & \text{CH}_3\text{Cl} \\ 0 & 0 & 0 & 0 & \text{CH}_2\text{Cl}_2 \\ 0 & 0 & 0 & 1 & \text{CHCl}_3 \\ -1 & 4 & -6 & 4 & \text{CCl}_4 \end{bmatrix} = \text{CH}_4 + \text{CCl}_4 + 6\text{CH}_2\text{Cl}_2 - 4\text{CH}_3\text{Cl} - 4\text{CHCl}_3 = 0$$

The enthalpy change of this GA RER is

$$\Delta H(g) = \Delta H(\text{CH}_4, \text{CH}_3\text{Cl}, \text{CH}_2\text{Cl}_2, \text{CHCl}_3, \text{CCl}_4) = \begin{bmatrix} 1 & 0 & 0 & 0 & -17.8 \\ 0 & 1 & 0 & 0 & -20.0 \\ 0 & 0 & 0 & 0 & -22.8 \\ 0 & 0 & 0 & 1 & -24.6 \\ -1 & 4 & -6 & 4 & -22.9 \end{bmatrix} = 0.9 \text{ kcal/mol}$$

As can be seen, the enthalpy change of this GA RER is smaller than the enthalpy changes of the GA RERs obtained within the first approximation. This result means that the second approximation results in a more accurate estimation of the enthalpy of formation of the species. In particular, the errors are as follows:

$$\Delta_f H_{298}^\circ(\text{CH}_4)_{\text{exp}} - \Delta_f H_{298}^\circ(\text{CH}_4)_{\text{calc}} = \frac{0.9}{1} = 0.9 \text{ kcal/mol}$$

$$\Delta_f H_{298}^\circ(\text{CH}_3\text{Cl})_{\text{exp}} - \Delta_f H_{298}^\circ(\text{CH}_3\text{Cl})_{\text{calc}} = -\frac{0.9}{4} = 0.25 \text{ kcal/mol}$$

$$\Delta_f H_{298}^\circ(\text{CH}_2\text{Cl}_2)_{\text{exp}} - \Delta_f H_{298}^\circ(\text{CH}_2\text{Cl}_2)_{\text{calc}} = \frac{0.9}{6} = 0.15 \text{ kcal/mol}$$

$$\Delta_f H_{298}^\circ(\text{CHCl}_3)_{\text{exp}} - \Delta_f H_{298}^\circ(\text{CHCl}_3)_{\text{calc}} = -\frac{0.9}{4} = -0.25 \text{ kcal/mol}$$

$$\Delta_f H_{298}^\circ(\text{CCl}_4)_{\text{exp}} - \Delta_f H_{298}^\circ(\text{CCl}_4)_{\text{calc}} = \frac{0.9}{1} = 0.9 \text{ kcal/mol}$$

Notice again that the GA methods work better for the intermediate chlorinated methanes.

6. Discussion and Concluding Remarks

From the above-described development, it follows that the conventional formalism provided by the theory of RERs can be naturally extended to include additional constraints. Thus, one can define and generate a stoichiometrically unique and finite set of RERs that additionally preserve the number and types of groups. This new type of RER, referenced here as the GA RER, provides a deeper insight into the conventional GA methods. In particular, assuming that the main assumptions of the GA methods are exactly valid should result in GA RERs that have the remarkable property of being thermoneutral. This observation allows an alternative formulation of the GA methods, in terms of GA RERs. Namely, it has been proved that the changes in the thermodynamic functions of the GA RERs are related in a simple manner to the error of the GA methods. As a result, the error of the GA methods, as well as the thermodynamic properties of the species, may be easily evaluated without any knowledge of the GA increments. The GA RER approach also reveals the existence of a strong interrelation between the stoichiometry of the system and the accuracy of the GA methods. Thus, it appears that the higher the stoichiometric coefficient of a species in a GA RER, the higher the accuracy of the GA predictions for that particular species. The immediate consequence of this finding is that, on the basis of a purely stoichiometric analysis, one might predict the species whose thermodynamic properties may be evaluated with the highest accuracy.

Appendix

Proof of Eq 14. Substituting eqs 3 and 5 into the first and last columns in eq 13, respectively, gives

$$\Delta H(g) = \begin{vmatrix} \sum_{j=1}^s a_{j1}\beta_{i_1j} + \sum_{k=1}^p b_{k1}g_{i_1,k} & \Gamma_{i_1,2} & \dots & \Gamma_{i_1,q} & \sum_{r=1}^p g_{i_1,r}\Delta_f H_{298}^{\circ}(g_r) \\ \sum_{i=1}^s a_{j1}\beta_{i_2j} + \sum_{k=1}^p b_{k1}g_{i_2,k} & \Gamma_{i_2,2} & \dots & \Gamma_{i_2,q} & \sum_{r=1}^p g_{i_2,r}\Delta_f H_{298}^{\circ}(g_r) \\ \dots & \dots & \dots & \dots & \dots \\ \sum_{i=1}^s a_{j1}\beta_{i_qj} + \sum_{k=1}^p b_{k1}g_{i_q,k} & \Gamma_{i_q,2} & \dots & \Gamma_{i_q,q} & \sum_{r=1}^p g_{i_q,r}\Delta_f H_{298}^{\circ}(g_r) \\ \sum_{i=1}^s a_{j1}\beta_{i_{q+1}j} + \sum_{k=1}^p b_{k1}g_{i_{q+1},k} & \Gamma_{i_{q+1},2} & \dots & \Gamma_{i_{q+1},q} & \sum_{r=1}^p g_{i_{q+1},r}\Delta_f H_{298}^{\circ}(g_r) \end{vmatrix}$$

$$= \begin{vmatrix} \sum_{j=1}^s a_{j1}\beta_{i_1j} & \Gamma_{i_1,2} & \dots & \Gamma_{i_1,q} & \sum_{r=1}^p g_{i_1,r}\Delta_f H_{298}^{\circ}(g_r) \\ \sum_{j=1}^s a_{j1}\beta_{i_2j} & \Gamma_{i_2,2} & \dots & \Gamma_{i_2,q} & \sum_{r=1}^p g_{i_2,r}\Delta_f H_{298}^{\circ}(g_r) \\ \dots & \dots & \dots & \dots & \dots \\ \sum_{j=1}^s a_{j1}\beta_{i_qj} & \Gamma_{i_q,2} & \dots & \Gamma_{i_q,q} & \sum_{r=1}^p g_{i_q,r}\Delta_f H_{298}^{\circ}(g_r) \\ \sum_{j=1}^s a_{j1}\beta_{i_{q+1}j} & \Gamma_{i_{q+1},2} & \dots & \Gamma_{i_{q+1},q} & \sum_{r=1}^p g_{i_{q+1},r}\Delta_f H_{298}^{\circ}(g_r) \end{vmatrix} + \begin{vmatrix} \sum_{k=1}^p b_{k1}g_{i_1,k} & \Gamma_{i_1,2} & \dots & \Gamma_{i_1,q} & \sum_{r=1}^p g_{i_1,r}\Delta_f H_{298}^{\circ}(g_r) \\ \sum_{k=1}^p b_{k1}g_{i_2,k} & \Gamma_{i_2,2} & \dots & \Gamma_{i_2,q} & \sum_{r=1}^p g_{i_2,r}\Delta_f H_{298}^{\circ}(g_r) \\ \dots & \dots & \dots & \dots & \dots \\ \sum_{k=1}^p b_{k1}g_{i_q,k} & \Gamma_{i_q,2} & \dots & \Gamma_{i_q,q} & \sum_{r=1}^p g_{i_q,r}\Delta_f H_{298}^{\circ}(g_r) \\ \sum_{k=1}^p b_{k1}g_{i_{q+1},k} & \Gamma_{i_{q+1},2} & \dots & \Gamma_{i_{q+1},q} & \sum_{r=1}^p g_{i_{q+1},r}\Delta_f H_{298}^{\circ}(g_r) \end{vmatrix}$$

The second determinant may be presented as

$$\begin{vmatrix}
 \sum_{k=1}^p b_{k1} g_{i_1,k} & \Gamma_{i_1,2} & \dots & \Gamma_{i_1,q} & \sum_{r=1}^p g_{i_1,r} \Delta_f H_{298}^\circ(g_r) \\
 \sum_{k=1}^p b_{k1} g_{i_2,k} & \Gamma_{i_2,2} & \dots & \Gamma_{i_2,q} & \sum_{r=1}^p g_{i_2,r} \Delta_f H_{298}^\circ(g_r) \\
 \dots & \dots & \dots & \dots & \dots \\
 \sum_{k=1}^p b_{k1} g_{i_q,k} & \Gamma_{i_q,2} & \dots & \Gamma_{i_q,q} & \sum_{r=1}^p g_{i_q,r} \Delta_f H_{298}^\circ(g_r) \\
 \sum_{k=1}^p b_{k1} g_{i_{q+1},k} & \Gamma_{i_{q+1},2} & \dots & \Gamma_{i_{q+1},q} & \sum_{r=1}^p g_{i_{q+1},r} \Delta_f H_{298}^\circ(g_r)
 \end{vmatrix}
 = \sum_{k=1}^p \sum_{r=1}^p b_{k1} \Delta_f H_{298}^\circ(g_r)
 \begin{vmatrix}
 g_{i_1,k} & \Gamma_{i_1,2} & \dots & \Gamma_{i_1,q} & g_{i_1,r} \\
 g_{i_2,k} & \Gamma_{i_2,2} & \dots & \Gamma_{i_2,q} & g_{i_2,r} \\
 \dots & \dots & \dots & \dots & \dots \\
 g_{i_q,k} & \Gamma_{i_q,2} & \dots & \Gamma_{i_q,q} & g_{i_q,r} \\
 g_{i_{q+1},k} & \Gamma_{i_{q+1},2} & \dots & \Gamma_{i_{q+1},q} & g_{i_{q+1},r}
 \end{vmatrix}$$

It is seen that because

$$\begin{vmatrix}
 g_{i_1,k} & \Gamma_{i_1,2} & \dots & \Gamma_{i_1,q} & g_{i_1,r} \\
 g_{i_2,k} & \Gamma_{i_2,2} & \dots & \Gamma_{i_2,q} & g_{i_2,r} \\
 \dots & \dots & \dots & \dots & \dots \\
 g_{i_q,k} & \Gamma_{i_q,2} & \dots & \Gamma_{i_q,q} & g_{i_q,r} \\
 g_{i_{q+1},k} & \Gamma_{i_{q+1},2} & \dots & \Gamma_{i_{q+1},q} & g_{i_{q+1},r}
 \end{vmatrix}
 = 0 \quad (\text{for } k = r)$$

and

$$\begin{vmatrix}
 g_{i_1,k} & \Gamma_{i_1,2} & \dots & \Gamma_{i_1,q} & g_{i_1,r} \\
 g_{i_2,k} & \Gamma_{i_2,2} & \dots & \Gamma_{i_2,q} & g_{i_2,r} \\
 \dots & \dots & \dots & \dots & \dots \\
 g_{i_q,k} & \Gamma_{i_q,2} & \dots & \Gamma_{i_q,q} & g_{i_q,r} \\
 g_{i_{q+1},k} & \Gamma_{i_{q+1},2} & \dots & \Gamma_{i_{q+1},q} & g_{i_{q+1},r}
 \end{vmatrix}
 = -
 \begin{vmatrix}
 g_{i_1,r} & \Gamma_{i_1,2} & \dots & \Gamma_{i_1,q} & g_{i_1,k} \\
 g_{i_2,r} & \Gamma_{i_2,2} & \dots & \Gamma_{i_2,q} & g_{i_2,k} \\
 \dots & \dots & \dots & \dots & \dots \\
 g_{i_q,r} & \Gamma_{i_q,2} & \dots & \Gamma_{i_q,q} & g_{i_q,k} \\
 g_{i_{q+1},r} & \Gamma_{i_{q+1},2} & \dots & \Gamma_{i_{q+1},q} & g_{i_{q+1},k}
 \end{vmatrix}
 \quad (\text{for } k \neq r)$$

we have

$$\begin{vmatrix}
 \sum_{k=1}^p b_{k1} g_{i_1,k} & \Gamma_{i_1,2} & \dots & \Gamma_{i_1,q} & \sum_{r=1}^p g_{i_1,r} \Delta_f H_{298}^\circ(g_r) \\
 \sum_{k=1}^p b_{k1} g_{i_2,k} & \Gamma_{i_2,2} & \dots & \Gamma_{i_2,q} & \sum_{r=1}^p g_{i_2,r} \Delta_f H_{298}^\circ(g_r) \\
 \dots & \dots & \dots & \dots & \dots \\
 \sum_{k=1}^p b_{k1} g_{i_q,k} & \Gamma_{i_q,2} & \dots & \Gamma_{i_q,q} & \sum_{r=1}^p g_{i_q,r} \Delta_f H_{298}^\circ(g_r) \\
 \sum_{k=1}^p b_{k1} g_{i_{q+1},k} & \Gamma_{i_{q+1},2} & \dots & \Gamma_{i_{q+1},q} & \sum_{r=1}^p g_{i_{q+1},r} \Delta_f H_{298}^\circ(g_r)
 \end{vmatrix}
 = 0 \tag{A1}$$

Repeating the same treatment with the second column, we have

$$\begin{aligned}
\Delta H(g) &= \begin{vmatrix} \sum_{j=1}^s a_{j1}\beta_{i_1j} & \Gamma_{i_1,2} & \dots & \Gamma_{i_1,q} & \sum_{r=1}^p g_{i_1,r}\Delta_r H_{298}^\circ(g_r) \\ \sum_{j=1}^s a_{j1}\beta_{i_2j} & \Gamma_{i_2,2} & \dots & \Gamma_{i_2,q} & \sum_{r=1}^p g_{i_2,r}\Delta_r H_{298}^\circ(g_r) \\ \dots & \dots & \dots & \dots & \dots \\ \sum_{j=1}^s a_{j1}\beta_{i_qj} & \Gamma_{i_q,2} & \dots & \Gamma_{i_q,q} & \sum_{r=1}^p g_{i_q,r}\Delta_r H_{298}^\circ(g_r) \\ \sum_{j=1}^s a_{j1}\beta_{i_{q+1}j} & \Gamma_{i_{q+1},2} & \dots & \Gamma_{i_{q+1},q} & \sum_{r=1}^p g_{i_{q+1},r}\Delta_r H_{298}^\circ(g_r) \end{vmatrix} \\
&= \begin{vmatrix} \sum_{j=1}^s a_{j1}\beta_{i_1j} & \sum_{j=1}^s a_{j2}\beta_{i_1j} + \sum_{k=1}^p b_{k2}g_{i_1,k} & \dots & \Gamma_{i_1,q} & \sum_{r=1}^p g_{i_1,r}\Delta_r H_{298}^\circ(g_r) \\ \sum_{j=1}^s a_{j1}\beta_{i_2j} & \sum_{j=1}^s a_{j2}\beta_{i_2j} + \sum_{k=1}^p b_{k2}g_{i_2,k} & \dots & \Gamma_{i_2,q} & \sum_{r=1}^p g_{i_2,r}\Delta_r H_{298}^\circ(g_r) \\ \dots & \dots & \dots & \dots & \dots \\ \sum_{j=1}^s a_{j1}\beta_{i_qj} & \sum_{j=1}^s a_{j2}\beta_{i_qj} + \sum_{k=1}^p b_{k2}g_{i_q,k} & \dots & \Gamma_{i_q,q} & \sum_{r=1}^p g_{i_q,r}\Delta_r H_{298}^\circ(g_r) \\ \sum_{j=1}^s a_{j1}\beta_{i_{q+1}j} & \sum_{j=1}^s a_{j2}\beta_{i_{q+1}j} + \sum_{k=1}^p b_{k2}g_{i_{q+1},k} & \dots & \Gamma_{i_{q+1},q} & \sum_{r=1}^p g_{i_{q+1},r}\Delta_r H_{298}^\circ(g_r) \end{vmatrix} \\
&= \begin{vmatrix} \sum_{j=1}^s a_{j1}\beta_{i_1j} & \sum_{j=1}^s a_{j2}\beta_{i_1j} & \dots & \Gamma_{i_1,q} & \sum_{r=1}^p g_{i_1,r}\Delta_r H_{298}^\circ(g_r) \\ \sum_{j=1}^s a_{j1}\beta_{i_2j} & \sum_{j=1}^s a_{j2}\beta_{i_2j} & \dots & \Gamma_{i_2,q} & \sum_{r=1}^p g_{i_2,r}\Delta_r H_{298}^\circ(g_r) \\ \dots & \dots & \dots & \dots & \dots \\ \sum_{j=1}^s a_{j1}\beta_{i_qj} & \sum_{j=1}^s a_{j2}\beta_{i_qj} & \dots & \Gamma_{i_q,q} & \sum_{r=1}^p g_{i_q,r}\Delta_r H_{298}^\circ(g_r) \\ \sum_{j=1}^s a_{j1}\beta_{i_{q+1}j} & \sum_{j=1}^s a_{j2}\beta_{i_{q+1}j} & \dots & \Gamma_{i_{q+1},q} & \sum_{r=1}^p g_{i_{q+1},r}\Delta_r H_{298}^\circ(g_r) \end{vmatrix} + \begin{vmatrix} \sum_{j=1}^s a_{j1}\beta_{i_1j} & \sum_{k=1}^p b_{k2}g_{i_1,k} & \dots & \Gamma_{i_1,q} & \sum_{r=1}^p g_{i_1,r}\Delta_r H_{298}^\circ(g_r) \\ \sum_{j=1}^s a_{j1}\beta_{i_2j} & \sum_{k=1}^p b_{k2}g_{i_2,k} & \dots & \Gamma_{i_2,q} & \sum_{r=1}^p g_{i_2,r}\Delta_r H_{298}^\circ(g_r) \\ \dots & \dots & \dots & \dots & \dots \\ \sum_{j=1}^s a_{j1}\beta_{i_qj} & \sum_{k=1}^p b_{k2}g_{i_q,k} & \dots & \Gamma_{i_q,q} & \sum_{r=1}^p g_{i_q,r}\Delta_r H_{298}^\circ(g_r) \\ \sum_{j=1}^s a_{j1}\beta_{i_{q+1}j} & \sum_{k=1}^p b_{k2}g_{i_{q+1},k} & \dots & \Gamma_{i_{q+1},q} & \sum_{r=1}^p g_{i_{q+1},r}\Delta_r H_{298}^\circ(g_r) \end{vmatrix}
\end{aligned}$$

The last two determinants are equal to zero for the same reasons as those for the determinant in eq A1.

Note Added after ASAP Posting: This article was released ASAP on 3/8/2003 with an error in eq 4. The correct version was posted on 3/11/2003.

References and Notes

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