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A General Thermodynamic and Stoichiometric Theory of Stability of Chemical Species

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A new approach to the evaluation of stability of chemical species is proposed. The main idea is to allow the species to conceptually interact via a special type of chemical reaction so that an equilibrium state is achieved. Additionally, the energies of the species are allowed to vary from their initial (standard) to their equilibrium values so that the energy change of any conceivable reaction at equilibrium is equal to zero. The equilibrium energies of the species are further evaluated using an optimization procedure similar to that of the least-squares method. A species is considered unstable if the difference between its initial and equilibrium energy is positive (the species releases energy). On the contrary, if the difference between the initial and the equilibrium energy of a species is negative, the species is stable (the species absorbs energy). This type of stability of species is referred to as the overall stability. Employing the response reactions (RERs) formalism, one shows further that the overall stabilities of the species may be partitioned into different types of contributions. In particular, it is shown that the conventional definition of stability of the species is just an appropriately normalized part of the overall stability.

Introduction

The relative stabilities of a given class of species are normally evaluated on the basis of stoichiometric and thermochemical considerations. In particular, one of the simplest and most often employed procedures is as follows. First, an appropriate set of reference species is selected.[1] Next, a certain type of reaction involving each test species and reference species, along with their energy (enthalpy) changes, is generated.[2,3] Finally, the energy (enthalpy) changes of the reactions are normalized to a common characteristic of the test species, e.g., energy (enthalpy) change of the reaction per atom, per mole, per ring, per π electron, etc.[4] In many cases, the evaluation of the relative stabilities of the species employing the procedure briefly outlined above gives correct results. There are cases, however, when the predicted relative stabilities of the species are completely erroneous.

The following two simple examples illustrate the procedure. Thus, it is well-known that the relative stabilities of alkanes C_nH_{2n+2} decrease as n increases. This *correct statement* is normally proved on the basis of the enthalpies of formation of alkanes. In other words, the reference species are C(gr) and H_2(g), whereas the respective chemical reactions are conventional formation reactions. Further, the enthalpies of formation are normalized to one mole of carbon. For instance, for the first four alkanes we have (kJ/mol)[5]

$$\begin{array}{llll}
 & \Delta H^0_{f,i} & \Delta H^0_{f,i}/n & \\
C(gr) + H_2(g) = CH_4(g) & -74.9 & -74.9 & (i) \\
2C(gr) + 3H_2(g) = C_2H_6(g) & -83.8 & -41.9 & (ii) \\
3C(gr) + 4H_2(g) = C_3H_8(g) & -104.7 & -34.9 & (iii) \\
4C(gr) + 5H_2(g) = C_4H_{10}(g) & -125.6 & -31.4 & (iv)
\end{array}$$

Because the enthalpy changes per mole of carbon in these formation reactions increase it may be concluded that the order of stability of the first four alkanes is

$$CH_4(g) > C_2H_6(g) > C_3H_8(g) > C_4H_{10}(g)$$

It may be noticed that the same result is obtained if enthalpies of formation are normalized to 1 mol of hydrogen.

As a second example, let us consider the evaluation of the homodesmotic resonance energy (RE) of benzene and coronene.[6] In this case, the reference species are ethylene and butadiene, whereas the chemical reactions are referred to as homodesmotic reactions. To determine the relative stabilities of benzene and coronene, the enthalpy changes of the homodesmotic reactions are further normalized to one π electron. The results are (kJ/mol)[6]

$$\begin{array}{llll}
 & \Delta H^0_j & \Delta H^0_j/\pi e & \\
3H_2C{=}CH{-}CH{=}CH_2 \rightarrow & & & \\
\quad 3H_2C{=}CH_2 + \text{benzene} & -89.9 & -15.0 & (v) \\
18H_2C{=}CH{-}CH{=}CH_2 \rightarrow & & & \\
\quad 24H_2C{=}CH_2 + \text{coronene} & -418.0 & -17.4 & (vi)
\end{array}$$

On the basis of these stoichiometric and thermochemical considerations, it is concluded[6] that coronene is more stable than benzene; i.e., coronene is more aromatic than benzene. This conclusion, however, *is wrong*, that is, the situation is just the opposite! A rigorous quantitative proof of this statement is presented below. Here, we consider only a brief qualitative analysis. The energy (enthalpy) change of any chemical reaction reflects the *overall* difference in enthalpy (energy) between the reactants and products. Thus, from reaction v it follows that 3 mol of ethylene plus 1 mol of benzene at standard conditions are more stable than 3 mol of butadiene by 89.9 kJ. Similarly, from reaction vi it follows that 24 mol of ethylene plus 1 mol of coronene are more stable than 18 mol of butadiene by 418

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kJ. If reaction v is multiplied by 6 and reaction vi is multiplied by −1 and both reactions are added, we obtain

$$\text{coronene} + 6\text{H}_2\text{C}{=}\text{CH}_2 \rightarrow 6\text{benzene} \qquad \Delta H^0_{\text{vii}} = -121.4 \text{ kJ/mol} \quad \text{(vii)}$$

From this relation it may be concluded that 6 mol of benzene are more stable than 1 mol of coronene and 6 mol of ethylene by 121.4 kJ. Similarly, multiplying reaction v by 8 and reaction vi by −1 and adding them we have

$$\text{coronene} + 6\text{H}_2\text{C}{=}\text{CH}{-}\text{CH}{=}\text{CH}_2 \rightarrow 8\text{benzene} \qquad \Delta H^0_{\text{viii}} = -301.2 \text{ kJ/mol} \quad \text{(viii)}$$

Thus, 8 mol of benzene are more stable that 1 mol of coronene and 6 mol of butadiene by 301.2 kJ. Now, an energy (enthalpy) balance for benzene and coronene over reactions v−viii clearly shows that benzene is more stable than coronene. Indeed, the huge stability of coronene in reaction vi, i.e., −418 kJ, is compensated by its instability in reactions vii and viii, i.e., 121.4 kJ + 301.2 kJ = 421.4 kJ. On the other hand, the modest stability of benzene in reaction v, i.e., −89.9 kJ, is substantially increased by its stability in reactions vii and viii, i.e., −6 × 121.4 kJ − 8 × 301.2 kJ = −3138.0 kJ. From these simple considerations, it is seen that the evaluation of the relative stabilities of species based exclusively on direct comparison of the energy (enthalpy) changes of single reactions involving test and reference species is inadequate and can result in erroneous conclusions.

There is a tacit assumption in the literature that the relative stabilities of chemical species are determined mainly by the selection of the reference species (stable with respect to what?) and thermochemistry of the species (how much?). This point of view especially persists in evaluating more subtle types of relative stabilities of species such as resonance and strain energies. Though the choice of the reference species and their thermochemistry is decisive, the relative stabilities of species may be significantly affected by an inappropriate account for their stoichiometry. In many cases, failure to appropriately account for the stoichiometric factor may cause serious errors. Thus, in the first example discussed above, the stoichiometric factor is small and the order of relative stability of the species is not affected. In the second example, however, the stoichiometric factor is dominant and neglecting it causes a serious error.

In this work we present a new approach to the evaluation of the stability of chemical species. This approach follows directly from our previous results that chemical thermodynamics, stoichiometry and the least-squares method are interrelated.[7−9] More specifically, we propose a new rigorous definition, an algorithm of evaluation, and a remarkable interpretation of the stability of chemical species. The approach is general and valid for any type of stability.

Notation and Definitions

We consider a set of p chemical species $B_1, B_2, ..., B_p$. Each of the species is characterized by a standard thermodynamic quantity E^0_i ($i = 1, 2, ..., p$) that is appropriate to describe the species stability, e.g., standard enthalpy of formation $\Delta H^0_{f,i}$, total ab initio enthalpy H^0_i, standard Gibbs free energy of formation $\Delta G^0_{f,i}$, etc. For simplicity, in what follows, the quantity E^0_i ($i = 1, 2, ..., p$) is referred to as the standard energy, or, simply, energy. It is thus convenient to define the vectors

$$\mathbf{B} = (B_1, B_2, ..., B_p)^T \tag{1}$$

$$\mathbf{E}^0 = (E^0_i, E^0_2, ..., E^0_p)^T \tag{2}$$

Let g_j ($j = 1, 2, ..., s$) be a set of structural units from which the species can be assembled. In particular, g_j may represent the atoms, bonds, groups in Benson's sense, etc.[10] Because a group can be always associated with an atom, bond, etc., in what follows by structural unit we mean a group. Further, let g_{ij} be the number of groups g_j in the species B_i. We thus can define the matrix

$$\mathbf{g}' = \begin{bmatrix} g_{11} & g_{12} & ... & g_{1s} \\ g_{21} & g_{22} & ... & g_{2s} \\ ... & ... & ... & ... \\ g_{p1} & g_{p2} & ... & g_{ps} \end{bmatrix}$$

Often rank $\mathbf{g}' = q < s$. In such cases, the linearly dependent columns in $\mathbf{g}'$ may be dropped so that we can define a submatrix

$$\mathbf{g} = \begin{bmatrix} g_{11} & g_{12} & ... & g_{1q} \\ g_{21} & g_{22} & ... & g_{2q} \\ ... & ... & ... & ... \\ g_{p1} & g_{p2} & ... & g_{pq} \end{bmatrix} \tag{3}$$

such that rang $\mathbf{g} = q$. The submatrix $\mathbf{g}$ is referred to as the *group* matrix.

Next, we define and generate a set of linearly independent chemical reactions involving species $B_1, B_2, ..., B_p$

$$\rho = \boldsymbol{\nu}\mathbf{B} = \mathbf{0} \tag{4}$$

where $\boldsymbol{\rho}$ is the reaction vector

$$\rho = (\rho_1, \rho_2, ..., \rho_m)^T \tag{5}$$

and $\boldsymbol{\nu}$ is the stoichiometric matrix

$$\boldsymbol{\nu} = \begin{bmatrix} \nu_{11} & \nu_{12} & ... & \nu_{1p} \\ \nu_{21} & \nu_{22} & ... & \nu_{2p} \\ ... & ... & ... & ... \\ \nu_{m1} & \nu_{m2} & ... & \nu_{mp} \end{bmatrix} \tag{6}$$

By analogy with the conventional chemical stoichiometry matrix $\boldsymbol{\nu}$ may be derived from

$$\boldsymbol{\nu}\mathbf{g} = \mathbf{0} \tag{7}$$

In other words the chemical reactions $\boldsymbol{\rho}$ are required to preserve the type and number of groups. For this reason it is appropriate to call them group additivity (GA) reactions. Obviously, when the groups are associated with atoms, bonds, etc., the GA reactions are equivalent to conventional reactions, isodesmic reactions, homodesmotic reactions, etc. As well-known from linear algebra, the number of linearly independent solutions of eq 7, i.e., the number of linearly independent GA reactions $\boldsymbol{\rho}$, is equal to $m = p -$ rank $\mathbf{g} = p - q$.[11] An arbitrary set of linearly independent reactions $\boldsymbol{\rho}$ may be generated by solving eq 7 using any appropriate procedure.

Finally, define the vector

$$\Delta\mathbf{E}^0 = (\Delta E_1^0, \Delta E_2^0, ..., \Delta E_m^0)^{\mathrm{T}} \tag{8}$$

where ΔE_j^0 ($j = 1, 2, ..., m$) are the energy changes of the GA reactions ρ_j ($j = 1, 2, ..., m$). From chemical thermodynamics it is known that $\mathbf{E}^0$ and $\Delta\mathbf{E}^0$ are interrelated via

$$\Delta\mathbf{E}^0 = \boldsymbol{\nu}\mathbf{E}^0 \tag{9}$$

A New Definition of the Stability of Chemical Species

Our approach to the evaluation of stability of chemical species may be formulated as follows. We define an initial state of the system such that the species B_i ($i = 1, 2, ..., p$) are characterized by their standard energies E_i^0 ($i = 1, 2, ..., p$). We further allow the species to react according to reactions 4, thus arriving at an equilibrium state of the system. At the same time, the energies of the species are assumed to vary from their standard values E_i^0 ($i = 1, 2, ..., p$) to their equilibrium values, E_i^{eq} ($i = 1, 2, ..., p$). Thus, we define the vectors

$$\mathbf{E}^{\mathrm{eq}} = (E_1^{\mathrm{eq}}, E_2^{\mathrm{eq}}, ..., E_p^{\mathrm{eq}})^{\mathrm{T}} \tag{10}$$

$$\mathbf{S} = \mathbf{E}^0 - \mathbf{E}^{\mathrm{eq}} = (E_1^0 - E_1^{\mathrm{eq}}, E_2^0 - E_2^{\mathrm{eq}}, ..., E_p^0 - E_p^{\mathrm{eq}})^{\mathrm{T}} \tag{11}$$

When $S_i = E_i^0 - E_i^{\mathrm{eq}} > 0$, the species B_i possesses an excess of energy as compared to the equilibrium state. As a result, the energy of species B_i decreases during the reaction; i.e., species B_i releases energy. On the contrary, if $S_i = E_i^0 - E_i^{\mathrm{eq}} < 0$, species B_i has a deficit of energy as compared to the equilibrium state. In this case, the energy of species B_i increases during the reaction; i.e., species B_i accumulates energy. On the basis of these considerations, the stability/instability criterion in a chemical system comprising species B_i ($i = 1, 2, ..., p$) is defined as

(a) Species B_i is unstable if $S_i = E_i^0 - E_i^{\mathrm{eq}} > 0$
(b) Species B_i is stable if $S_i = E_i^0 - E_i^{\mathrm{eq}} < 0$
(c) Species B_i is at equilibrium if $S_i = E_i^0 - E_i^{\mathrm{eq}} = 0$

For reasons that will become clear later on, the vector **S** is referred to as the *overall stability vector*.

Quantitative Evaluation of the Overall Stability of Species

Obviously, to be able to evaluate the overall stabilities of the species, i.e., the vector **S**, it is necessary to evaluate the vector $\mathbf{E}^{\mathrm{eq}}$. This can be done by requiring that at equilibrium the energy changes of the GA reactions $\boldsymbol{\rho}$ are equal to zero, i.e.,

$$\boldsymbol{\nu}\mathbf{E}^{\mathrm{eq}} = 0 \tag{12}$$

Combining eqs 12 and 9 we have

$$\boldsymbol{\nu}\mathbf{S} = \Delta\mathbf{E}^0 \tag{13}$$

Now, the overall stability vector **S** may be evaluated by minimizing the product $\mathbf{S}^{\mathrm{T}}\mathbf{S}$ subject to the constraints given by eq 13. The procedure has been described in detail elsewhere. The result is[7]

$$\mathbf{S} = \boldsymbol{\nu}^{\mathrm{T}}(\boldsymbol{\nu}\boldsymbol{\nu}^{\mathrm{T}})^{-1}\Delta\mathbf{E}^0 \tag{14}$$

Notice that although the stoichiometric matrix $\boldsymbol{\nu}$ is generated arbitrarily, the overall stability vector **S** is unique. In other words, **S** is independent of the choice of $\boldsymbol{\nu}$.

Overall Stability of the Species in Terms of Response Reactions

Equation 14 has precisely the same mathematical form and, consequently, the same properties as the equations considered in our previous work.[7−9] In particular, we have shown that such thermodynamic and stoichiometric relations can be uniquely partitioned into a sum of contributions associated with a special class of reactions, referred to as response reactions (RERs).[12] Because this result is crucial to our analysis, we consider briefly the partition of **S** into contributions coming from RERs. Clearly, in our case, these are GA RERs. Following the general RERs formalism, we, thus, define a GA RER as a reaction that involves no more than rank $\mathbf{g} + 1 = q + 1$ species. Let these $q + 1$ species be $\mathrm{B}_{i_1}, \mathrm{B}_{i_2}, ..., \mathrm{B}_{i_q}, \mathrm{B}_{i_{q+1}}$, where $i_1, i_2, ..., i_q, i_{q+1}$ is a set of integers satisfying the condition $1 \le i_1 < i_2 < ... < i_q < i_{q+1} \le p$. A GA RER is denoted by $g = g(\mathrm{B}_{i_1}, \mathrm{B}_{i_2}, ..., \mathrm{B}_{i_q}, \mathrm{B}_{i_{q+1}})$, thus specifying the species involved in this particular GA RER. Technical details of the enumeration of GA RERs are presented in the Appendix. Further, let $\nu_i(g)$ be the stoichiometric coefficient of species B_i and $\Delta E(g)$ the energy change of a particular GA RER. Then, the overall species stabilities S_i ($i = 1, 2, ..., p$) may be partitioned into contributions coming from GA RERs according to

$$S_i = \frac{1}{D}\sum_g \nu_i(g)\, \Delta E^0(g) \qquad i = 1, 2, ..., p \tag{15}$$

where

$$D = \frac{1}{m}\sum_g \sum_{k=1}^{n} \nu_k^{\,2}(g) \tag{16}$$

Because the GA RERs are stoichiometrically unique, the independence of the overall stability vector **S** on the choice of $\boldsymbol{\nu}$ is self-evident.

Interpretation of the Overall Stability of Species

In view of eq 15, the overall stability of the species S_i ($i = 1, 2, ..., p$) has a remarkable chemical meaning. Namely, the overall stability may be uniquely partitioned into a sum of contributions associated with GA RERs. Each of these contributions has a simple form; i.e., it is equal to the product between the stoichiometric coefficient of the species in the GA RER, $\nu_i(g)$, and the energy change of the GA RER, $\Delta E^0(g)$. Notice that the sign of the product $\nu_i(g)\, \Delta E^0(g)$ is independent of the direction of the GA RER. Because the sum in eq 15 runs over a complete set of GA RERs and the latter are stoichiometrically unique, the overall stability of the species represents a unique stoichiometry and energy balance. Besides, the overall stabilities of the species are appropriately normalized. Indeed, the function D in eq 15 is the same for all species and may be treated as a common normalization factor.

To appreciate other major consequences of the overall stability of the species, let us partition the list of species B_i ($i = 1, 2, ..., p$) into n reference B_i ($i = 1, 2, ..., n$) and $p - n$ test B_i ($i = n + 1, n + 2, ..., p$) species. Consider, for instance, the overall stability of the test species B_{n+1}. According to eq 15, the overall stability of B_{n+1} is a sum of contributions coming from all of the GA RERs involving species B_{n+1}, i.e., a sum of contributions coming from GA RERs $g = g(\mathrm{B}_{i_1}, \mathrm{B}_{i_2}, ..., \mathrm{B}_{i_q}, \mathrm{B}_{n+1})$. These GA

RERs may be further partitioned into three types. The first type involves the species B_{n+1} and q reference species, i.e., $g = g(B_{i_1}, B_{i_2}, ..., B_{i_q}, B_{n+1})$ where $1 \le i_1 < i_2 < ... < i_q \le n$. The second type of GA RERs involves the species B_{n+1} and a variable number of both reference and test species, i.e., $g = g(B_{i_1}, B_{i_2}, ..., B_{i_x}, B_{i_{x+1}}, B_{i_{x+2}}, ..., B_{i_q}, B_{n+1})$ where $1 \le i_1 < i_2 < ... < i_x \le n$ and $n + 1 < i_{x+1} < i_{x+2} < ... < i_q \le p$. Finally, the third type of GA RERs involves the species B_{n+1} and q test species, i.e., $g = g(B_{i_1}, B_{i_2}, ..., B_{i_q}, B_{n+1})$ where $n + 1 < i_1 < i_2 < ... < i_q \le p$. Correspondingly, the overall stability of the species B_{n+1} may be partitioned into three different types of contributions. The first type of contributions comes solely from the interaction of B_{n+1} with the reference species B_i ($i = 1, 2, ..., n$). The second type of contributions is a mixed one, that is, comprises interactions between the species B_{n+1} and a mixed set of reference B_i ($i = 1, 2, ..., n$) and test B_i ($i = n + 2, n + 3, ..., p$) species. The third type of contributions include interactions between the species B_{n+1} and the remaining test species B_i ($i = n + 2, n + 3, ..., p$). To distinguish among these types of contributions, it is appropriate to call them *relative*, *mixed*, and *direct* stabilities. Thus, in the general case, the overall stabilities S_{n+j} ($j = 1, 2, ..., p - n$) of the test species B_{n+j} ($j = 1, 2, ..., p - n$) may be partitioned into relative ($S_{n+j}{}^{r}$), mixed (S^{m}_{n+j}), and direct (S^{d}_{n+j}) stabilities

$$S_{n+j} = S^{r}_{n+j} + S^{m}_{n+j} + S^{d}_{n+j} \qquad j = 1, 2, ..., p - n \quad (17)$$

The above interpretation reveals that the overall stability of chemical species is the most exhaustive one in that it takes into account all of the possible interactions among species. More importantly, however, eq 17 shows that several narrower definitions of stability may be proposed. These are described next.

Relative Stability of the Species

Most often in the literature by stability of the species is meant the relative stability. The latter can be evaluated by neglecting the last two terms in eq 17, i.e., considering only the relative stability of the test species, S^{r}_{n+j} ($j = 1, 2, ..., p - n$). In this case, the stability of each test species B_{n+j} ($j = 1, 2, ..., p - n$) is evaluated *separately* with respect to reference species B_i ($i = 1, 2, ..., n$). In other words, the relative stabilities of the test species B_{n+j} ($j = 1, 2, ..., p - n$) represent their overall stabilities evaluated in $p - n$ separate subsystems ($B_1, B_2, ..., B_n, B_{n+1}$), ($B_1, B_2, ..., B_n, B_{n+2}$), ..., ($B_1, B_2, ..., B_n, B_p$). In particular, when the number of reference species n is such that there is only one possible reaction between any test and reference species, i.e., $n = q$, the relative stabilities of the test species B_{q+j} ($j = 1, 2, ..., p - q$) is given by a simple relation. Thus, let the only GA reaction in the subsystem ($B_1, B_2, ..., B_q, B_{q+j}$) be

$$\rho_j = \nu_{j1}B_1 + \nu_{j2}B_2 + ... + \nu_{jq}B_q + \nu_{j,q+j}B_{q+j} = 0 \qquad j = 1, 2, ..., p - q \quad (18)$$

Obviously, this reaction is a GA RER (it involves no more than $q + 1$ species). Under these conditions, according to eq 15 the relative stabilities of the test species B_{q+j} ($j = 1, 2, ..., p - q$) are given by

$$S^{r}_{q+j} = \frac{1}{D^{r}_{q+j}} \Delta E^{0}_{j} \qquad j = 1, 2, ..., p - n \quad (19)$$

where ΔE^{0}_{j} is the energy change of reaction 18 and D^{r}_{q+j} is the normalization factor

$$D^{r}_{q+j} = \frac{\nu_{j,q+j}}{{\nu_{j1}}^2 + {\nu_{j2}}^2 + ... + {\nu_{jq}}^2 + {\nu_{j,q+j}}^2} \qquad j = 1, 2, ..., p - q \quad (20)$$

Direct Stability of the Species

Another useful option in evaluating the stabilities of the species is to neglect the first two terms in eq 17. That is, to consider the stabilities of the test species directly with respect to each other. In other words, the direct stabilities S^{d}_{n+j} ($j = 1, 2, ..., p - n$) of the test species B_{n+j} ($j = 1, 2, ..., p - n$) are equal to the overall stabilities in the subsystem ($B_{n+1}, B_{n+2}, ..., B_p$). Clearly, such stability is meaningful only if the number of test species, $p - n$, exceeds the rank of the group matrix q.

Conventional vs Overall Stability of the Species

On the basis of the above interpretation, it is easy now to figure out what is the interrelation between the conventional and the overall stabilities of the species. The conventional stabilities of the species are normally defined as the relative stabilities of the test species B_{n+j} ($j = 1, 2, ..., p - n$) with respect to reference species B_i ($i = 1, 2, ..., n$). In other words, the conventional stabilities are the relative stabilities in the current terminology. At the same time, there is a substantial difference between the conventional and relative stabilities. To be able to formulate this difference quantitatively, consider two separate cases. First, let the number of reference species B_i ($i = 1, 2, ..., n$) be $n = q$. In other words, the number of reference species is such that there is only one possible GA reaction between a given test species B_{q+j} ($j = 1, 2, ..., p - q$) and the reference species B_i ($i = 1, 2, ..., q$). This reaction is given by eq 18. In this case, the conventional stabilities, denoted by S^{c}_{q+j}, are just the energy changes of the GA reaction per one mole of the test species B_{q+j} ($j = 1, 2, ..., p - q$)

$$S^{c}_{q+j} = \frac{1}{\nu_{j,q+j}} \Delta E^{0}_{j} \qquad j = 1, 2, ..., p - q \quad (21)$$

These conventional stabilities are often further normalized to a certain characteristic of the test species, such as, the number of atoms, bonds, rings, π electrons, etc. Comparing eq 21 with eq 19 it can be seen that the difference between the conventional, S^{c}_{q+j}, and relative, S^{r}_{q+j}, stabilities is due to different ways of normalization. More specifically, the relative stability, S^{r}_{q+j}, eq 19, refers to the entire GA reaction whereas the conventional stability, S^{c}_{q+j}, eq 21, refers to one mole of the test species.

Another distinct case is $n > q + 1$, that is, the number of possible GA reactions between a given test species and the reference species exceeds one. Under these conditions the conventional stabilities of the test species, S^{c}_{n+j}, are defined only with respect to "equilibrated" reference species. It means that the equilibrium energies E^{eq}_{i} ($i = 1, 2, ..., n$) of the reference species B_i ($i = 1, 2, ..., n$) are evaluated *separately*; i.e., the test species B_{n+j} ($j = 1, 2, ..., p - n$) are completely eliminated from the "equilibration" process. In this case, as shown by us recently,[9] the conventional stabilities are equal to the energy changes of arbitrary GA reactions involving test and reference species. In particular, if the arbitrary GA reactions are chosen as GA RERs, $g = g(B_{i_1}, B_{i_2}, ..., B_{i_q}, B_{n+1})$ where $1 \leq i_1 < i_2 < ... < i_q \leq n$, then the conventional stabilities are given by[9]

$$S^{c}_{n+j} = \frac{1}{\nu_{n+j}(g)}\Delta E^0(g) = \frac{1}{\nu_{n+j}(g)}\begin{vmatrix} g_{i_1,1} & g_{i_1,2} & ... & g_{i_1,q} & E^{eq}_{i1} \\ g_{i_2,1} & g_{i_2,2} & ... & g_{i_2,q} & E^{eq}_{i2} \\ ... & ... & ... & ... & ... \\ g_{i_q,1} & g_{i_q,2} & ... & g_{i_q,q} & E^{eq}_{iq} \\ g_{n+j,1} & g_{n+j,2} & ... & g_{n+j,q} & E^{0}_{n+j} \end{vmatrix} \quad (22)$$

$$j = 1, 2, ..., p - n$$

where

$$\nu_{n+j}(g) = \begin{vmatrix} g_{i_1,1} & g_{i_2,2} & ... & g_{i_1,q} \\ g_{i_2,1} & g_{i_2,2} & ... & g_{i_2,q} \\ ... & ... & ... & ... \\ g_{i_q,1} & g_{i_q,2} & ... & g_{i_q,q} \end{vmatrix} \neq 0 \quad (23)$$

Again, the conventional stabilities refer to 1 mol of the test species. On the contrary, the relative stabilities refer to the entire system.

Examples

The theoretical developments presented above are next illustrated with the help of examples. The examples were selected so as to cover a large variety of applications from different areas.

Stabilities of Alkanes. *Overall Stabilities.* Consider the overall stabilities of the first four alkanes with respect to C(gr) and H_2(g). In this case the system comprises $p = 6$ species including $n = 2$ two reference species, B_1 = C(gr) and $B_2 = H_2$(g), and $p - n = 4$ test species, namely, $B_3 = CH_4$(g), $B_4 = C_2H_6$(g), $B_5 = C_3H_8$(g), and $B_6 = C_4H_{10}$(g). Obviously, the GA matrix is just the formula matrix, i.e., g_1 = C, $g_2 = H_2$:

$$\mathbf{g} = \begin{array}{c} \begin{array}{cc} C & H_2 \end{array} \\ \begin{pmatrix} 1 & 0 \\ 0 & 1 \\ 1 & 2 \\ 2 & 3 \\ 3 & 4 \\ 4 & 5 \end{pmatrix} \end{array} \begin{array}{l} \\ B_1 \\ B_2 \\ B_3 \\ B_4 \\ B_5 \\ B_6 \end{array}$$

Further, the GA reactions in this system are conventional chemical reactions whereas the GA RERs are conventional RERs. The energies are equal to the enthalpies of formation of B_1, B_2, B_3, B_4, B_5, and B_6 and are, respectively 0, 0, −79.4, −83.8, −104.7, and −125.6 kJ/mol.[5] First, we generate a set of linearly independent reactions. Because rank $\mathbf{g}$ = 2 the number of linearly independent reactions is equal to $m = p -$ rank $\mathbf{g} = 6-2 = 4$. These can be selected, for instance, as formation reactions

$$\rho_1 = -B_1 - 2B_2 + B_3 = 0 \qquad \Delta E^0_1 = \Delta H^0_1 = -74.9 \text{ kJ/mol}$$

$$\rho_2 = -2B_1 - 3B_2 + B_4 = 0 \qquad \Delta E^0_2 = \Delta H^0_2 = -83.8 \text{ kJ/mol}$$

$$\rho_3 = -3B_1 - 4B_2 + B_5 = 0 \qquad \Delta E^0_3 = \Delta H^0_3 = -104.7 \text{ kJ/mol}$$

$$\rho_4 = -4B_1 - 5B_2 + B_6 = 0 \qquad \Delta E^0_4 = \Delta H^0_4 = -125.6 \text{ kJ/mol}$$

The stoichiometric matrix and the energy (enthalpy) change vector are thus equal to

$$\boldsymbol{\nu} = \begin{array}{c} \begin{array}{cccccc} B_1 & B_2 & B_3 & B_4 & B_5 & B_6 \end{array} \\ \begin{bmatrix} -1 & -2 & 1 & 0 & 0 & 0 \\ -2 & -3 & 0 & 1 & 0 & 0 \\ -3 & -4 & 0 & 0 & 1 & 0 \\ -4 & -5 & 0 & 0 & 0 & 1 \end{bmatrix} \end{array} \begin{array}{l} \\ \rho_1 \\ \rho_2 \\ \rho_3 \\ \rho_4 \end{array}$$

$$\Delta \mathbf{E}^0 = \Delta \mathbf{H}^0 = \begin{pmatrix} -74.9 \\ -83.8 \\ -104.7 \\ -125.6 \end{pmatrix}$$

Substituting these relations into eq 14 and performing the respective matrix operations we obtain

$$S_1 = 3.1 \text{ kJ/mol} \qquad S_4 = -5.4 \text{ kJ/mol}$$

$$S_2 = 24.1 \text{ kJ/mol} \qquad S_5 = 0.9 \text{ kJ/mol}$$

$$S_3 = -23.6 \text{ kJ/mol} \qquad S_6 = 7.2 \text{ kJ/mol}$$

It is seen that methane (B_3) and ethane (B_4) are the only stable species. Notice also that the order of stability of alkanes is $CH_4(g) > C_2H_6(g) > C_3H_8(g) > C_4H_{10}(g)$.

Let us now analyze the overall stabilities in this system in terms of RERs. Because rank $\mathbf{g}$ = 2 a GA RER in this system involves 2 + 1 = 3 species. That is, any three species from a total of six define a GA RER. Consequently, the number of GA RERs is equal to 6!/3!/3! = 20. For instance, the species B_1, B_3, and B_4 define the following GA RER

$$g(B_1,B_3,B_4) = \begin{vmatrix} 1 & 0 & B_1 \\ 1 & 2 & B_3 \\ 2 & 3 & B_4 \end{vmatrix} = -B_1 - 3B_3 + 2B_4 = 0$$

Similarly, the enthalpy change of this GA RER is

$$\Delta H^0(g) = \begin{vmatrix} 1 & 0 & 0 \\ 1 & 2 & -74.9 \\ 2 & 3 & -83.8 \end{vmatrix} = 57.1 \text{ kJ/mol}$$

A complete list of GA RERs along with their enthalpy changes is presented in Table 1. As can be seen, the GA RERs may be further partitioned into three subsets. Thus, each of the first four GA RERs involves only one test species and, hence, the contributions coming from these GA RERs may be regarded as the relative stabilities of the species. The next 12 GA RERs involve two test and one reference species; i.e., the contributions associated with these GA RERs represent the mixed contribution to the stabilities of the species. Finally, each of the last four GA RERs involve only test species; that is, the contributions

TABLE 1: A Complete List of RERs Involving C(gr), H_2(g), and the First Four Alkanes

RERs	ΔH(g), kJ/mol
1. $g(B_1, B_2, B_3) = -B_1 - 2B_2 + B_3 = 0$	−74.9
2. $g(B_1, B_2, B_4) = -2B_1 - 3B_2 + B_4 = 0$	−83.8
3. $g(B_1, B_2, B_5) = -3B_1 - 4B_2 + B_5 = 0$	−104.7
4. $g(B_1, B_2, B_6) = -4B_1 - 5B_2 + B_6 = 0$	−125.6
5. $g(B_1, B_3, B_4) = -B_1 - 3B_3 + 2B_4 = 0$	57.1
6. $g(B_1, B_3, B_5) = -2B_1 - 4B_3 + 2B_5 = 0$	90.2
7. $g(B_1, B_3, B_6) = -3B_1 - 5B_3 + 2B_6 = 0$	123.3
8. $g(B_1, B_4, B_5) = -B_1 - 4B_4 + 3B_5 = 0$	21.1
9. $g(B_1, B_4, B_6) = -2B_1 - 5B_4 + 3B_6 = 0$	42.2
10. $g(B_1, B_5, B_6) = -B_1 - 5B_5 + 4B_6 = 0$	21.1
11. $g(B_2, B_3, B_4) = -B_2 + 2B_3 - B_4 = 0$	−66.0
12. $g(B_2, B_3, B_5) = -2B_2 + 3B_3 - B_5 = 0$	−120.0
13. $g(B_2, B_3, B_6) = -3B_2 + 4B_3 - B_6 = 0$	−174.0
14. $g(B_2, B_4, B_5) = -B_2 + 3B_4 - 2B_5 = 0$	−42.0
15. $g(B_2, B_4, B_6) = -2B_2 + 4B_4 - 2B_6 = 0$	−84.0
16. $g(B_2, B_5, B_6) = -B_2 + 4B_5 - 3B_6 = 0$	−42.0
17. $g(B_3, B_4, B_5) = -B_3 + 2B_4 - B_5 = 0$	12.0
18. $g(B_3, B_4, B_6) = -2B_3 + 3B_4 - B_6 = 0$	24.0
19. $g(B_3, B_5, B_6) = -B_3 + 3B_5 - 2B_6 = 0$	12.0
20. $g(B_4, B_5, B_6) = -B_4 + 2B_5 - B_6 = 0$	0.0

coming from these GA RERs comprise the direct stabilities of the test species. As an example, consider the partition of the overall stability of propane (B_5) into contributions associated with GA RERs. Thus, employing eqs 15 and 16 and the data from Table 1, the overall stability of B_5 may be partitioned into contributions coming from GA RERs as

$$S_5 = \frac{1}{105}(-104.7 + 2 \times 90.2 + 3 \times 21.1 - 5 \times 21.1 + 120.0 + 2 \times 42.0 - 4 \times 42.0 - 12.0 + 3 \times 12.0 + 1 \times 0) = 0.9 \text{ kJ/mol}$$

where 105 is the normalization factor D, eq 16. As can be seen, propane (B_5) is stable according to some GA RERs, i.e.,

$$3. \quad g(B_1, B_2, B_5) = -3B_1 - 4B_2 + B_5 = 0 \qquad \Delta H^0(g) = -104.7 \text{ kJ/mol}$$

$$10. \quad g(B_1, B_5, B_6) = -B_1 - 5B_5 + 4B_6 = 0 \qquad \Delta H^0(g) = 21.1 \text{ kJ/mol}$$

$$16. \quad g(B_2, B_5, B_6) = -B_2 + 4B_5 - 3B_6 = 0 \qquad \Delta H^0(g) = -42.0 \text{ kJ/mol}$$

$$17. \quad g(B_3, B_4, B_5) = -B_3 + 2B_4 - B_5 = 0 \qquad \Delta H^0(g) = 12.0 \text{ kJ/mol}$$

unstable according to other GA RERs, i.e.,

$$6. \quad g(B_1, B_3, B_5) = -2B_1 - 4B_3 + 2B_5 = 0 \qquad \Delta H^0(g) = 90.2 \text{ kJ/mol}$$

$$8. \quad g(B_1, B_4, B_5) = -B_1 - 4B_4 + 3B_5 = 0 \qquad \Delta H^0(g) = 21.1 \text{ kJ/mol}$$

$$12. \quad g(B_2, B_3, B_5) = -2B_2 + 3B_3 - B_5 = 0 \qquad \Delta H^0(g) = -120.0 \text{ kJ/mol}$$

$$14. \quad g(B_2, B_4, B_5) = -B_2 + 3B_4 - 2B_5 = 0 \qquad \Delta H^0(g) = -42.0 \text{ kJ/mol}$$

$$19. \quad g(B_3, B_5, B_6) = -B_3 + 3B_5 - 2B_6 = 0 \qquad \Delta H^0(g) = 12.0 \text{ kJ/mol}$$

and neutral according to one GA RER, i.e.,

$$20. \quad g(B_4, B_5, B_6) = -B_4 + 2B_5 - B_6 = 0 \qquad \Delta H^0(g) = 0.0 \text{ kJ/mol}$$

Overall, however, in this particular system, propane is unstable.

Relative Stabilities. Consider now the relative stabilities of the first four alkanes, that is, the separate stabilities with respect to reference species, i.e., B_1 = C(gr) and $B_2 = H_2$(g). According to the definition, the relative stabilities of alkanes are equal to the overall stabilities in four separate subsystems, i.e., (B_1, B_2, B_3), (B_1, B_2, B_4), (B_1, B_2, B_5), and (B_1, B_2, B_6). Because there is only one reaction in each subsystem, we can employ eqs 19 and 20. We thus have

$$\text{(i)} \quad \rho_1 = -B_1 - 2B_2 + B_3 = 0 \qquad \Delta E_1^0 = \Delta H_1^0 = -74.9 \text{ kJ/mol}$$

$$S_3^r = \frac{(+1)(-74.9)}{1 + 4 + 1} = -12.5 \text{ kJ/mol}$$

$$\text{(ii)} \quad \rho_2 = -2B_1 - 3B_2 + B_4 = 0 \qquad \Delta E_2^0 = \Delta H_2^0 = -83.8 \text{ kJ/mol}$$

$$S_4^r = \frac{(+1)(-83.8)}{4 + 9 + 1} = -6.0 \text{ kJ/mol}$$

$$\text{(iii)} \quad \rho_3 = -3B_1 - 4B_2 + B_5 = 0 \qquad \Delta E_3^0 = \Delta H_3^0 = -104.7 \text{ kJ/mol}$$

$$S_5^r = \frac{(+1)(-104.7)}{9 + 16 + 1} = -4.0 \text{ kJ/mol}$$

$$\text{(iv)} \quad \rho_4 = -4B_1 - 5B_2 + B_6 = 0 \qquad \Delta E_4^0 = \Delta H_4^0 = -125.6 \text{ kJ/mol}$$

$$S_5^r = \frac{(+1)(-125.6)}{16 + 25 + 1} = -3.0 \text{ kJ/mol}$$

Hence, the first four alkanes are stable with respect to reference species whereas their relative stabilities decrease as the molecular mass increases.

Direct Stabilities. Finally, let us analyze the direct stabilities of the first four alkanes, that is, their stabilities relative to each other. By definition, the direct stabilities are equal to the overall stabilities in the subsystem comprising only the test species. In our case this is the subsystem (B_3, B_4, B_5, B_6). From the formula matrix it is readily deduced that the number of linearly independent reactions in this subsystem is equal to 2. An arbitrary set of such reactions may be selected, for instance, as

$$\rho_5 = -B_3 + 2B_4 - B_5 = 0 \qquad \Delta E_5^0 = \Delta H_5^0 = 12.0 \text{ kJ/mol}$$

$$\rho_6 = -2B_3 + 3B_4 - B_6 = 0 \qquad \Delta E_6^0 = \Delta H_6^0 = 24.0 \text{ kJ/mol}$$

The stoichiometric matrix and energy change vector are

$$\boldsymbol{\nu} = \begin{array}{c} \begin{array}{cccc} B_3 & B_4 & B_5 & B_6 \end{array} \\ \begin{bmatrix} -1 & 2 & -1 & 0 \\ -2 & 3 & 0 & -1 \end{bmatrix} \end{array} \begin{array}{c} \\ \rho_5 \\ \rho_6 \end{array} \qquad \mathbf{\Delta E}^0 = \mathbf{\Delta H}^0 = \begin{pmatrix} 12.0 \\ 24.0 \end{pmatrix}$$

Substituting $\boldsymbol{\nu}$ into eq 14 and performing the necessary matrix operations, we obtain

$$S_3^{\mathrm{d}} = -3.6\ \text{kJ/mol} \qquad S_5^{\mathrm{d}} = 1.2\ \text{kJ/mol}$$

$$S_4^{\mathrm{d}} = 4.8\ \text{kJ/mol} \qquad S_6^{\mathrm{d}} = -2.4\ \text{kJ/mol}$$

Thus, in this subsystem, methane (B_3) and butane (B_6) are stable whereas ethane (B_4) and propane (B_5) are unstable. Notice that the order of direct stabilities of alkanes differs from the order of overall and relative stability. More insights into these results may be obtained on the basis of the decomposition of the direct stabilities into contributions associated with GA RERs (last four GA RERs in Table 1).

Stabilities (Homodesmotic Stabilization Energies) of Benzene and Coronene. As mentioned in the Introduction, the conventional approach to the evaluation of the homodesmotic stabilization energies (HSE) may result in serious errors. Next, we analyze the evaluation of the HSE for benzene and coronene.[6] For this system, we have two reference species, i.e., B_1 = ethylene and B_2 = butadiene and two test species, i.e., B_3 = benzene and B_4 = coronene.

Overall Stabilities. The reactions defining the HSE for benzene and coronene, eqs v and vi, are linearly independent and, hence, can be directly used to evaluate the overall stabilities of the species. Employing the above notation of the species these reactions may be written as

$$\rho_1 = 3B_1 - 3B_2 + B_3 = 0 \qquad \Delta E_1^0 = \Delta H_1^0 = -89.9\ \text{kJ/mol}$$

$$\rho_2 = 24B_1 - 18B_2 + B_4 = 0$$

$$\Delta E_2^0 = \Delta H_2^0 = -418.0\ \text{kJ/mol}$$

This gives the following stoichiometric matrix and energy changes vector

$$\boldsymbol{\nu} = \begin{array}{cccc|c} B_1 & B_2 & B_3 & B_4 & \\ 3 & -3 & 1 & 0 & \rho_1 \\ 24 & -18 & 0 & 1 & \rho_2 \end{array} \qquad \Delta\mathbf{E}^0 = \Delta\mathbf{H}^0 = \begin{pmatrix} -89.9 \\ -418.0 \end{pmatrix}$$

Substituting $\boldsymbol{\nu}$ and $\Delta\mathbf{E}^0$ into eq 14 and performing the respective matrix operations gives

$$S_1 = -3.0\ \text{kJ/mol} \qquad S_3 = -22.8\ \text{kJ/mol}$$

$$S_2 = 19.4\ \text{kJ/mol} \qquad S_4 = 2.7\ \text{kJ/mol}$$

Thus, the most stable species in this system is benzene (B_3) and not coronene (B_4) as stated in ref 6. Moreover, overall, coronene (B_4) is even unstable in this system.

This behavior of the system may be easily rationalized by partitioning the overall stabilities of the species into contributions coming from GA RERs. The latter may be obtained either from the group matrix or by linearly combing the set of linearly independent GA reactions, i.e., ρ_1 and ρ_2. For simplicity, let us generate the GA RERs starting from ρ_1 and ρ_2. By definition (see Appendix) a GA RER may be generated by linearly combing $m = 2$ linearly independent GA reactions so as to eliminate at least $m - 1 = 2 - 1 = 1$ species. Thus, the total number of GA RERs in this system is equal to the number of ways 1 species may be selected from a total of $p = 4$ species, i.e., $4!/1!/3! = 4$. For instance, if we eliminate B_1, the generated GA RER will involve B_2, B_3, and B_4

$$g'(B_1) = g(B_2, B_3, B_4) = \begin{vmatrix} 3 & \rho_1 \\ 24 & \rho_2 \end{vmatrix} = -24\rho_1 + 3\rho_2 = 18B_2 - 24B_3 + 3B_4 = 0$$

The energy (enthalpy) change of this GA RER is

$$\Delta H^0(g') = \Delta H^0(g) = \begin{vmatrix} 3 & \Delta H_1^0 \\ 24 & \Delta H_2^0 \end{vmatrix} = -24\Delta H_1^0 + 3\Delta H_2^0 = 903.6\ \text{kJ/mol}$$

A complete list of GA RERs generated in this was is presented below

1. $g(B_1, B_2, B_3) = 3B_1 - 3B_2 + B_3 = 0$
   $\Delta E_1^0 = \Delta H_2^0 = -89.9\ \text{kJ/mol}$
2. $g(B_1, B_2, B_4) = 24B_1 - 18B_2 + B_4 = 0$
   $\Delta E_2^0 = \Delta H_2^0 = -418.0\ \text{kJ/mol}$
3. $g(B_1, B_3, B_4) = -18B_1 + 18B_3 - 3B_4 = 0$
   $\Delta E_3^0 = \Delta H_3^0 = -364.2\ \text{kJ/mol}$
4. $g(B_2, B_3, B_4) = 18B_2 - 24B_3 + 3B_4 = 0$
   $\Delta E_4^0 = \Delta H_4^0 = 903.6\ \text{kJ/mol}$

As can be seen, according to the first two GA RERs, $g(B_1, B_2, B_3)$ and $g(B_1, B_2, B_4)$, both benzene (B_3) and coronene (B_4) are stable with respect to ethylene (B_1) and butadiene (B_2). From the third GA RER, $g(B_1, B_3, B_4)$, it follows that benzene (B_3) is more stable than ethylene (B_1) and coronene (B_4). Finally, according to the fourth GA RER, $g(B_2, B_3, B_4)$, benzene (B_3) is more stable than butadiene (B_2) and coronene (B_4). An exact stoichiometric and thermochemical balance according to eq 15 gives

$$S_3 = \frac{1}{1243}(-89.9 - 18 \times 364.2 - 24 \times 903.6) = -22.8\ \text{kJ/mol}$$

$$S_4 = \frac{1}{1243}(-418.0 + 3 \times 364.2 + 3 \times 903.6) = 2.7\ \text{kJ/mol}$$

where 1243 is the normalization factor D, eq 16.

Relative Stabilities. The relative stabilities of benzene (B_3) and coronene (B_4) are equal to their overall stabilities in the subsystems (B_1, B_2, B_3) and (B_1, B_2, B_4), respectively. Because both of these subsystems may be described by only one GA reaction, the relative stabilities may be evaluated employing eqs 19 and 20. We thus have

(i) $\rho_1 = 3B_1 - 3B_2 + B_3 = 0$

$$\Delta E_1^0 = \Delta H_1^0 = -89.9\ \text{kJ/mol}$$

$$S_3^{\mathrm{r}} = \frac{(+1)(-89.9)}{9 + 9 + 1} = -4.7\ \text{kJ/mol}$$

(ii) $\rho_2 = 24B_1 - 18B_2 + B_4 = 0$

$$\Delta E_2^0 = \Delta H_2^0 = -418.0\ \text{kJ/mol}$$

$$S_3^{\mathrm{r}} = \frac{(+1)(-418.0)}{576 + 324 + 1} = -0.5\ \text{kJ/mol}$$

As expected, both, benzene (B_3) and coronene (B_4) are stable with respect to the reference species. However, benzene (B_3) is much more stable than coronene (B_4).

Direct Stabilities. Because the number of test species is less than 3, the direct stabilities of the test species cannot be evaluated.

Stabilities (Resonance Energies) of Linear Acenes. In a recent paper Schleyer et al.[13] calculated the resonance stabilization energies (RE) of linear acenes. The RE were assumed to be equal to the negative energy (enthalpy) changes of the reactions

$$n\ \text{1,3-cyclohexadiene} + \textit{trans}\text{-perhydroacene} = n\ \text{cyclohexene} + \text{acene} \quad (20)$$

where $n = 3, 5, 7, 9, 11, 13, 15$. The Schleyer et al. DFT results are summarized in Table 2 (for species notation, see Table 3). On the basis of these estimations it was concluded that the RE of linear acenes per πe is *essentially constant* along the series. We show below that this conclusion is incorrect.

Overall Stabilities. Because the reactions that define the RE are linearly independent, they can be used directly to evaluate the overall stability of the species in the system

$$\rho_1 = -3B_1 + 3B_2 - B_3 + B_4 = 0 \qquad \Delta E_1^0 = \Delta H_1^0 = -137.2\ \text{kJ/mol}$$

$$\rho_2 = -5B_1 + 5B_2 - B_5 + B_6 = 0 \qquad \Delta E_2^0 = \Delta H_2^0 = -250.2\ \text{kJ/mol}$$

$$\rho_3 = -7B_1 + 7B_2 - B_7 + B_8 = 0 \qquad \Delta E_3^0 = \Delta H_3^0 = -350.2\ \text{kJ/mol}$$

$$\rho_4 = -9B_1 + 9B_2 - B_9 + B_{10} = 0 \qquad \Delta E_4^0 = \Delta H_4^0 = -438.9\ \text{kJ/mol}$$

$$\rho_5 = -11B_1 + 11B_2 - B_{11} + B_{12} = 0 \qquad \Delta E_5^0 = \Delta H_5^0 = -533.9\ \text{kJ/mol}$$

$$\rho_6 = -13B_1 + 13B_2 - B_{13} + B_{14} = 0 \qquad \Delta E_6^0 = \Delta H_6^0 = -643.9\ \text{kJ/mol}$$

$$\rho_7 = -15B_1 + 15B_2 - B_{15} + B_{16} = 0 \qquad \Delta E_7^0 = \Delta H_7^0 = -734.3\ \text{kJ/mol}$$

Thus, the stoichiometric matrix and the energy changes vector are

$$\boldsymbol{\nu} = \begin{array}{cccccccccccccccc|c}
B_1 & B_2 & B_3 & B_4 & B_5 & B_6 & B_7 & B_8 & B_9 & B_{10} & B_{11} & B_{12} & B_{13} & B_{14} & B_{15} & B_{16} & \\
-3 & 3 & -1 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \rho_1 \\
-5 & 5 & 0 & 0 & -1 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \rho_2 \\
-7 & 7 & 0 & 0 & 0 & 0 & -1 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \rho_3 \\
-9 & 9 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & \rho_4 \\
-11 & 11 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 1 & 0 & 0 & 0 & 0 & \rho_5 \\
-13 & 13 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 1 & 0 & 0 & \rho_6 \\
-15 & 15 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 1 & \rho_7
\end{array}$$

$$\Delta\mathbf{E}^0 = \Delta\mathbf{H}^0 = (-137.2, -250.2, -350.2, -438.9, -533.9, -643.9, -734.3)^T$$

Substituting ν and $\Delta\mathbf{E}^0$ into eq 14 gives the overall species stabilities that are presented in Table 3. The results are quite surprising. For instance, benzene (B_4), which certainly is the most aromatic (stable) species in this system, appears to be unstable (antiaromatic). On the contrary, cyclohexene (B_2) is the most stable (aromatic) species in the system.

TABLE 2: Resonance Energies (RE) and Overall (S_i) and Relative Stabilities (S_i^r) of Linear Acenes (in kJ/mol)

	RE	RE/πe	S_i	S_i^r
benzene (B_4)	137.3	22.9	4.9	−6.9
naphthalene (B_6)	250.3	25.0	−2.6	−4.8
anthracene (B_8)	350.4	25.0	−3.6	−3.5
tetracene (B_{10})	438.7	24.4	1.3	−2.7
pentacene (B_{12})	534.1	24.3	2.6	−2.2
hexacene (B_{14})	644.2	24.7	−3.5	−1.9
heptacene (B_{16})	734.6	24.5	0.3	−1.6

TABLE 3: Species Notation and Overall Stabilities (S_i, kJ/mol) in Linear Acenes Example

	S_i
B_1, 1,3-cyclohexadiene	24.5
B_2, cyclohexene	−24.5
B_3, cyclohexane	−4.9
B_4, benzene	4.9
B_5, *trans*-perhydronaphthalene	2.6
B_6, naphthalene	−2.6
B_7, *trans*-perhydroanthracene	2.8
B_8, anthracene	−2.8
B_9, *trans*-perhydrotetracene	−1.3
B_{10}, tetracene	1.3
B_{11}, *trans*-perhydropentacene	−2.6
B_{12}, pentacene	2.6
B_{13}, *trans*-perhydrohexacene	3.5
B_{14}, hexacene	−3.5
B_{15}, *trans*-perhydroheptacene	−0.3
B_{16}, heptacene	0.3

To understand the reasons of such behavior, consider the partition of the overall stabilities of the species into contributions coming from GA RERs. In this case, the GA RERs may be generated from the set of linearly independent GA reactions, as briefly discussed in the Appendix. Because rank $\boldsymbol{\nu} = 7$, a GA RER may be obtained by linearly combining $\rho_1, \rho_2, ..., \rho_7$ so as to eliminate at least $7 - 1 = 6$ species. Alternatively, eliminating at least 6 species implies that a GA RER will involve no more than $16 - 6 = 10$ species. This means that the total number of GA RERs is equal to the number of ways 6 species may be selected from a total of 16, i.e., $16!/6!/10! = 8008$. The distinct number of GA RERs, however, is much smaller because of a substantial number of repetitions and "zero" GA RERs. Indeed, an inspection of $\boldsymbol{\nu}$ reveals that half of the columns differ by other half just by a factor of -1. That is, trying to eliminate concomitantly, e.g., species B_1 and B_2, will result in a "zero" GA RER, i.e., a GA RER in which all of the stoichiometric coefficients are equal to zero. Obviously, a "zero" GA RER has no effect on the stabilities of species. We thus conclude that to generate stoichiometrically distinct GA RERs, half of the columns in $\boldsymbol{\nu}$ may be disregarded. For instance, eliminating B_2, B_4, B_6, B_8, B_{10}, and B_{12} results in the following GA RER

$$g'(B_2, B_4, B_6, B_8, B_{10}, B_{12}) = g(B_1, B_3, B_5, B_7, B_9, B_{11}, B_{13}, B_{14}, B_{15}, B_{16})$$

$$\begin{vmatrix}
3 & 1 & 0 & 0 & 0 & 0 & \rho_1 \\
5 & 0 & 1 & 0 & 0 & 0 & \rho_2 \\
7 & 0 & 0 & 1 & 0 & 0 & \rho_3 \\
9 & 0 & 0 & 0 & 1 & 0 & \rho_4 \\
11 & 0 & 0 & 0 & 0 & 1 & \rho_5 \\
13 & 0 & 0 & 0 & 0 & 0 & \rho_6 \\
15 & 0 & 0 & 0 & 0 & 0 & \rho_7
\end{vmatrix} =$$

$$15\rho_6 - 13\rho_7 = -15B_{13} + 15B_{14} + 13B_{15} - 13B_{16} = 0$$

Similarly, the enthalpy change of this GA RER is equal to

$$\Delta H^0(g') = \Delta H^0(g) = \begin{vmatrix} 3 & 1 & 0 & 0 & 0 & 0 & \Delta H_1^0 \\ 5 & 0 & 1 & 0 & 0 & 0 & \Delta H_2^0 \\ 7 & 0 & 0 & 1 & 0 & 0 & \Delta H_3^0 \\ 9 & 0 & 0 & 0 & 1 & 0 & \Delta H_4^0 \\ 11 & 0 & 0 & 0 & 0 & 1 & \Delta H_5^0 \\ 13 & 0 & 0 & 0 & 0 & 0 & \Delta H_6^0 \\ 15 & 0 & 0 & 0 & 0 & 0 & \Delta H_7^0 \end{vmatrix} = 15\Delta H_6^0 - 13\Delta H_7^0 = -113.0 \text{ kJ/mol}$$

A complete list of stoichiometrically distinct GA RERs along with their enthalpy changes is presented in Table 4. On the basis of these data and by employing eq 15 let us analyze the stability of benzene (B_4), for instance. As can be seen from Table 4, benzene (B_4) is involved in 7 GA RERs. According to one of them, namely

$$1.\ -3B_1 + 3B_2 - B_3 + B_4 = 0 \qquad \Delta H_1^0 = -137.2 \text{ kJ/mol}$$

benzene (B_4) is stable. Notice, that this GA RER coincides with ρ_1, i.e., the reaction that is used to define the conventional RE. In all of the remaining GA RERs, however, benzene (B_4) is unstable

$$8.\ -5B_3 + 5B_4 + 3B_5 - 3B_6 = 0 \qquad \Delta H_8^0 = 64.4 \text{ kJ/mol}$$

$$9.\ -7B_3 + 7B_4 + 3B_7 - 3B_8 = 0 \qquad \Delta H_9^0 = 90.0 \text{ kJ/mol}$$

$$10.\ -9B_3 + 9B_4 + 3B_9 - 3B_{10} = 0 \qquad \Delta H_{10}^0 = 80.3 \text{ kJ/mol}$$

$$11.\ -11B_3 + 11B_4 + 3B_{11} - 3B_{12} = 0 \qquad \Delta H_{11}^0 = 92.1 \text{ kJ/mol}$$

$$12.\ -13B_3 + 13B_4 + 3B_{13} - 3B_{14} = 0 \qquad \Delta H_{12}^0 = 147.3 \text{ kJ/mol}$$

$$13.\ -15B_3 + 15B_4 + 3B_{15} - 3B_{16} = 0 \qquad \Delta H_{13}^0 = 144.4 \text{ kJ/mol}$$

A rigorous energetic and stoichiometric balance according to eq 15 gives

$$S_4 = \frac{1}{1360}(-137.2 + 5 \times 64.4 + 7 \times 90.0 + 9 \times 80.3 + 11 \times 92.1 + 13 \times 147.3 + 15 \times 144.4) = 4.9 \text{ kJ/mol}$$

where 1360 is the normalization factor D, eq 16.

Relative Stabilities. The relative stabilities of linear acenes may be evaluated by applying eq 19 to GA reactions ρ_1, ρ_2, ..., ρ_7. For instance, the relative stability of benzene is determined on the basis of ρ_1 and, according to eqs 19 and 20, is equal to

$$S_4^{\mathrm{r}} = \frac{(+1)(-137.2)}{9 + 9 + 1 + 1} = -6.9 \text{ kJ/mol}$$

Similar calculations for the remaining acenes are presented in the last column of Table 2. As expected, all of the linear acenes are stable with respect to the reference species. Their stabilities, however, *decrease* along the series.

TABLE 4: Complete List of Stoichiometrically Distinct GA RERs and Their Enthalpy Changes (ΔH_j, kJ/mol) in Linear Acenes Example[a]

GA RERs	ΔH_j
1. $-3B_1 + 3B_2 - B_3 + B_4 = 0$	−137.2
2. $-5B_1 + 5B_2 - B_5 + B_6 = 0$	−250.2
3. $-7B_1 + 7B_2 - B_7 + B_8 = 0$	−350.2
4. $-9B_1 + 9B_2 - B_9 + B_{10} = 0$	−438.5
5. $-11B_1 + 11B_2 - B_{11} + B_{12} = 0$	−533.9
6. $-13B_1 + 13B_2 - B_{13} + B_{14} = 0$	−643.9
7. $-15B_1 + 15B_2 - B_{15} + B_{16} = 0$	−734.3
8. $-5B_3 + 5B_4 + 3B_5 - 3B_6 = 0$	64.4
9. $-7B_3 + 7B_4 + 3B_7 - 3B_8 = 0$	90.0
10. $-9B_3 + 9B_4 + 3B_9 - 3B_{10} = 0$	80.3
11. $-11B_3 + 11B_4 + 3B_{11} - 3B_{12} = 0$	92.1
12. $-13B_3 + 13B_4 + 3B_{13} -3B_{14} = 0$	147.7
13. $-15B_3 + 15B_4 + 3B_{15} - 3B_{16} = 0$	144.4
14. $-7B_5 + 7B_6 + 5B_7 - 5B_8 = 0$	−0.4
15. $-9B_5 + 9B_6 + 5B_9 - 5B_{10} = 0$	−59.4
16. $-11B_5 + 11B_6 + 5B_{11} - 5B_{12} = 0$	−82.8
17. $-13B_5 + 13B_6 + 5B_{13} - 5B_{14} = 0$	−33.1
18. $-15B_5 + 15B_6 + 5B_{15} - 5B_{16} = 0$	−81.6
19. $-9B_7 + 9B_8 + 7B_9 - 7B_{10} = 0$	−82.4
20. $-11B_7 + 11B_8 + 7B_{11} - 7B_{12} = 0$	−115.1
21. $-13B_7 + 13B_8 + 7B_{13} - 7B_{14} = 0$	−45.2
22. $-15B_7 + 15B_8 + 7B_{15} - 7B_{16} = 0$	−113.0
23. $-11B_9 + 11B_{10} + 9B_{11} - 9B_{12} = 0$	−18.4
24. $-13B_9 +13B_{10} + 9B_{13} - 9B_{14} = 0$	95.0
25. $-15B_9 + 15B_{10} + 9B_{15} - 9B_{16} = 0$	31.4
26. $-13B_{11} + 13B_{12} + 11B_{13} - 11B_{14} = 0$	142.7
27. $-15B_{11} + 15B_{12} + 11B_{15} - 11B_{16} = 0$	69.0
28. $-15B_{13} + 15B_{14} + 13B_{15}$ - $13B_{16} = 0$	−113.0

[a] For species notation, see Table 3.

Direct Stabilities. Due to the stoichiometric particularity of the system, the evaluation of the direct stabilities of linear acenes is prohibited. The point is that within this selection of the reference species, there is no way to write a balanced GA reaction involving only the linear acenes.

Instabilities (Strain Energies) of Cycloalkanes. Finally, we illustrate the application of the theory presented above to the evaluation of the strain energy. As an example, we consider a simplified model of strain energy of the first four cycloalkanes. Conventionally, the strain energies of cycloalkanes are defined with respect to linear alkanes. To simplify the treatment, we select only five alkanes as reference species, namely, ethane (B_1), propane (B_2), butane (B_3), pentane (B_4), and hexane (B_5). The test species are: cyclopropane (B_6), cyclobutane (B_7), cyclopentane (B_8), and cyclohexane (B_9). Hence, we have a total of $p = 9$ species from which $n = 5$ are reference species and the remaining $p - n = 4$ are test species. We further employ the Benson group additivity approach. According to Benson, this particular system may be described by two types of groups, i.e., $g_1 = \mathrm{CH_3}$ and $g_2 = \mathrm{CH_2}$. Thus, the group matrix is

$$\mathbf{g} = \begin{array}{cc} g_1 & g_2 \\ \left(\begin{array}{cc} 2 & 0 \\ 2 & 1 \\ 2 & 2 \\ 2 & 3 \\ 2 & 4 \\ 0 & 3 \\ 0 & 4 \\ 0 & 5 \\ 0 & 6 \end{array}\right. & \left.\right) \end{array} \begin{array}{c} \\ B_1 \\ B_2 \\ B_3 \\ B_4 \\ B_5 \\ B_6 \\ B_7 \\ B_8 \\ B_9 \end{array} \approx \begin{array}{cc} g_1 & g_2 \\ \left(\begin{array}{cc} 1 & 0 \\ 1 & 1 \\ 1 & 2 \\ 1 & 3 \\ 1 & 4 \\ 0 & 3 \\ 0 & 4 \\ 0 & 5 \\ 0 & 6 \end{array}\right. & \left.\right) \end{array} \begin{array}{c} \\ B_1 \\ B_2 \\ B_3 \\ B_4 \\ B_5 \\ B_6 \\ B_7 \\ B_8 \\ B_9 \end{array} \qquad \text{rank } \mathbf{g} = 2$$

TABLE 5: Stabilities (Strain Energies) of Cycloalkanes: S_i^c (Conventional Stability), S_i (Overall Stability), S_i^r (Relative Stability), S_i^d (Direct Stability)[a]

	$\Delta H_{f,i}^0$	S_i^c	S_i	S_i^r	S_i^r	S_i^r	S_i^r	S_i^d
B_1, ethane	−83.8	0.04	19.8	36.6	34.5	8.1	0.6	
B_2, propane	−104.7	0.03	9.9	18.3	17.3	4.0	0.3	
B_3, butane	−125.6	0.02	0.0	0.0	0.0	0.0	0.0	
B_4, pentane	−146.8	−0.29	−10.2	−18.6	−17.5	−4.3	0.3	
B_5, hexane	−167.2	0.20	−19.6	−36.4	−34.2	−7.8	−0.4	
B_6, cyclopropane	53.1	115.5	86.1	60.9				98.3
B_7, cyclobutane	28.4	111.6	72.4		43.1			55.9
B_8, cyclopentane	−76.4	28.1	−21.4			8.0		−33.8
B_9, cyclohexane	−123.1	2.2	−57.1				0.5	−65.5

[a] All Energy Units, kJ/mol. Experimental Enthalpies of Formation From NIST Database.[5]

Notice that, to generate GA reactions with stoichiometric coefficients equal to the smallest integers, we divided all of the elements in the first column in **g** by 2. The energies of the species E_i ($i = 1, 2, ..., 9$) are equal to the experimental enthalpies of formation $\Delta H_{f,i}^0$ ($i = 1, 2, ..., 9$) and are presented in Table 5.

Conventional Stabilities. According to eq 22, to evaluate the conventional stabilities, it is necessary to know the equilibrium energies of the reference species, $E_i^{eq}(i = 1, 2, ..., 5)$. The latter need to be evaluated separately, i.e., excluding the test species. This can be done by, first, evaluating separately the overall stabilities of the reference species, S_i ($i = 1, 2, ..., 5$), and then, using eq 11, to find the equilibrium energies, i.e., $E_i^{eq} = E_i^0 - S_i(i = 1, 2, ..., 5)$. Because rank $\mathbf{g} = 2$, the number of linearly independent GA reactions among five reference species is equal to $5 - 2 = 3$. These may be selected, for instance, as

$$\rho_1 = B_1 - 2B_2 + B_3 = 0 \qquad \Delta E_1^0 = \Delta H_1^0 = 0.0 \text{ kJ/mol}$$

$$\rho_2 = 2B_1 - 3B_2 + B_4 = 0 \qquad \Delta E_2^0 = \Delta H_2^0 = -0.3 \text{ kJ/mol}$$

$$\rho_3 = 3B_1 - 4B_2 + B_5 = 0 \qquad \Delta E_3^0 = \Delta H_3^0 = 0.2 \text{ kJ/mol}$$

thus resulting in the following stoichiometric matrix and energy changes vector

$$\boldsymbol{\nu} = \begin{array}{c} \begin{array}{ccccc} B_1 & B_2 & B_3 & B_4 & B_5 \end{array} \\ \begin{bmatrix} 1 & -2 & 1 & 0 & 0 \\ 2 & -3 & 0 & 1 & 0 \\ 3 & -4 & 0 & 0 & 1 \end{bmatrix} \end{array} \begin{array}{c} \\ \rho_1 \\ \rho_2 \\ \rho_3 \end{array} \qquad \Delta\mathbf{E}^0 = \Delta\mathbf{H}^0 = \begin{pmatrix} 0.0 \\ -0.3 \\ 0.2 \end{pmatrix}$$

Substituting $\boldsymbol{\nu}$ and $\Delta\mathbf{E}^0$ in eq 14 gives

$$\mathbf{S} = (0.04, 0.03, 0.02, -0.29, 0.20)^T$$

Knowing **S** and $\mathbf{E}^0 = \Delta\mathbf{H}_f^0$, we can evaluate $\mathbf{E}^{eq}$

$$\mathbf{E}^{eq} = \mathbf{S} - \mathbf{E}^0 = (-83.84, -104.73, -125.62, -146.51, -167.40)^T$$

Now, the conventional stabilities of B_6, B_7, B_8, and B_9 may be evaluated according to eqs 22 and 23, i.e., as the energy (enthalpy) change of an arbitrary GA RER. Because rank $\mathbf{g} = 2$, a GA RER in this system involves no more than rank $\mathbf{g} + 1 = 2 + 1 = 3$ species. One of these species should be the test species whereas the remaining two species may be selected arbitrarily from the list of reference species. For instance, selecting the first two reference species B_1 and B_2 results in the following GA RER for B_6

$$g(B_1, B_2, B_6) = \begin{vmatrix} 1 & 0 & B_1 \\ 1 & 1 & B_2 \\ 0 & 3 & B_6 \end{vmatrix} = 3B_1 - 3B_2 + B_6 = 0$$

Hence, the conventional stability of B_6 is

$$S_6^c = \begin{vmatrix} 1 & 0 & E_1^{eq} \\ 1 & 1 & E_2^{eq} \\ 0 & 3 & E_6^0 \end{vmatrix} = \begin{vmatrix} 1 & 0 & -83.84 \\ 1 & 1 & -104.73 \\ 0 & 3 & 53.1 \end{vmatrix} = 115.47 \text{ kJ/mol}$$

Any other selection of two reference species will result in precisely the same stability. For instance, selecting B_1 and B_3 gives

$$g(B_1, B_3, B_6) = \begin{vmatrix} 1 & 0 & B_1 \\ 1 & 2 & B_3 \\ 0 & 3 & B_6 \end{vmatrix} = 3B_1 - 3B_3 + 2B_6 = 0$$

$$S_6^c = \frac{1}{2}\begin{vmatrix} 1 & 0 & E_1^{eq} \\ 1 & 2 & E_3^{eq} \\ 0 & 3 & E_6^0 \end{vmatrix} = \begin{vmatrix} 1 & 0 & -83.84 \\ 1 & 2 & -125.62 \\ 0 & 3 & 53.1 \end{vmatrix} = 115.47 \text{ kJ/mol}$$

Similar calculations for B_7, B_8, and B_9 give $S_7^c = 111.56$ kJ/mol, $S_8^c = 28.05$ kJ/mol, and $S_9^c = 2.24$ kJ/mol. Notice also that the stabilities of the test species are positive quantities; i.e., the test species are unstable (strained) with respect to reference species

Overall Stabilities. To evaluate the overall stabilities, we first generate an arbitrary set of linearly independent GA reactions involving both test (B_1, B_2, B_3, B_4, B_5) and reference (B_6, B_7, B_8, B_9) species, for instance

$$\rho_1 = B_1 - 2\,B_2 + B_3 = 0 \qquad \Delta E_1^0 = \Delta H_1^0 = 0.0 \text{ kJ/mol}$$

$$\rho_2 = 2B_1 - 3B_2 + B_4 = 0 \qquad \Delta E_2^0 = \Delta H_2^0 = -0.3 \text{ kJ/mol}$$

$$\rho_3 = 3B_1 - 4B_2 + B_5 = 0 \qquad \Delta E_3^0 = \Delta H_3^0 = 0.2 \text{ kJ/mol}$$

$$\rho_4 = 3B_1 - 3B_2 + B_6 = 0 \qquad \Delta E_4^0 = \Delta H_4^0 = 115.8 \text{ kJ/mol}$$

$$\rho_5 = 4B_1 - 4B_2 + B_7 = 0 \qquad \Delta E_5^0 = \Delta H_5^0 = 112.0 \text{ kJ/mol}$$

$$\rho_6 = 5B_1 - 5B_2 + B_8 = 0 \qquad \Delta E_6^0 = \Delta H_6^0 = 28.1 \text{ kJ/mol}$$

$$\rho_7 = 6B_1 - 6B_2 + B_9 = 0 \qquad \Delta E_7^0 = \Delta H_7^0 = 2.3 \text{ kJ/mol}$$

Thus

$$\boldsymbol{\nu} = \begin{array}{cccccccccc} B_1 & B_2 & B_3 & B_4 & B_5 & B_6 & B_7 & B_8 & B_9 & \\ 1 & -2 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & \rho_1 \\ 2 & -3 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & \rho_2 \\ 3 & -4 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & \rho_3 \\ 3 & -3 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & \rho_4 \\ 4 & -4 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & \rho_5 \\ 5 & -5 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & \rho_6 \\ 6 & -6 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & \rho_7 \end{array}$$

$$\Delta\mathbf{E}^0 = \Delta\mathbf{H}^0 = \begin{bmatrix} 0.0 \\ -0.3 \\ 0.2 \\ 115.8 \\ 112.0 \\ 28.1 \\ 2.3 \end{bmatrix}$$

The overall stabilities of the species calculated according to eq 14 are presented in Table 5. As expected, the most unstable (strained) species are cyclopropane (B_6) and cyclobutane (B_7). Interestingly, cyclopentane (B_8) and cyclohexane (B_9) are the most stable species in this system, i.e., more stable than the reference species.

Relative Stabilities. According to the above development, the relative stabilities of the test species B_6, B_7, B_8, and B_9 are equal to their overall stabilities in the subsystems (B_1, B_2, B_3, B_4, B_5, B_6), (B_1, B_2, B_3, B_4, B_5, B_7), (B_1, B_2, B_3, B_4, B_5, B_8), and (B_1, B_2, B_3, B_4, B_5, B_9), respectively. As an example, consider the relative stability of B_6. Our starting point is a set of linearly independent GA reactions, e.g.,

$$\rho_1 = B_1 - 2\,B_2 + B_3 = 0 \qquad \Delta E_1^0 = \Delta H_1^0 = 0.0 \text{ kJ/mol}$$

$$\rho_2 = 2B_1 - 3B_2 + B_4 = 0 \qquad \Delta E_2^0 = \Delta H_2^0 = -0.3 \text{ kJ/mol}$$

$$\rho_3 = 3B_1 - 4B_2 + B_5 = 0 \qquad \Delta E_3^0 = \Delta H_3^0 = 0.2 \text{ kJ/mol}$$

$$\rho_4 = 3B_1 - 3B_2 + B_6 = 0 \qquad \Delta E_4^0 = \Delta H_4^0 = 115.8 \text{ kJ/mol}$$

The stoichiometric matrix $\boldsymbol{\nu}$ and energy change vectors are

$$\boldsymbol{\nu} = \begin{array}{ccccccc} B_1 & B_2 & B_3 & B_4 & B_5 & B_6 & \\ 1 & -2 & 1 & 0 & 0 & 0 & \rho_1 \\ 2 & -3 & 0 & 1 & 0 & 0 & \rho_2 \\ 3 & -4 & 0 & 0 & 1 & 0 & \rho_3 \\ 3 & -3 & 0 & 0 & 0 & 1 & \rho_4 \end{array} \qquad \Delta\mathbf{E}^0 = \Delta\mathbf{H}^0 = \begin{bmatrix} 0.0 \\ -0.3 \\ 0.2 \\ 115.8 \end{bmatrix}$$

Employing eq 14, we obtain $S_6^{\mathrm{r}} = 60.9$ kJ/mol. Similar calculations for the remaining test species give (Table 5) $S_7^{\mathrm{r}} = 43.1$ kJ/mol, $S_8^{\mathrm{r}} = 8.0$ kJ/mol, and $S_9^{\mathrm{r}} = 0.5$ kJ/mol. Again, the instability (strain energy) decreases in the order cyclopropane (B_6) > cyclobutane (B_7) > cyclopentane (B_8) > cyclohexane (B_9). Notice that, numerically, the relative stabilities are less than the conventional stabilities.

Direct Stabilities. Finally, consider the direct stabilities of test species B_6, B_7, B_8, and B_9, i.e., their stabilities with respect to each other. Because all of the test species involve only one group, namely, $g_2 = CH_2$, the group matrix for the test species becomes

$$\mathbf{g} = \begin{array}{cc} g_2 & \\ 3 & B_6 \\ 4 & B_7 \\ 5 & B_8 \\ 6 & B_9 \end{array}$$

Thus, a GA reaction involves no more than rank $\mathbf{g} + 1 = 1 + 1 = 2$ species. An appropriate set of linearly independent GA reactions may be selected as

$$\rho_8 = -4B_6 + 3B_7 = 0 \qquad \Delta E_8^0 = \Delta H_8^0 = -127.2 \text{ kJ/mol}$$

$$\rho_9 = -5B_6 + 3B_8 = 0 \qquad \Delta E_9^0 = \Delta H_9^0 = -494.7 \text{ kJ/mol}$$

$$\rho_{10} = -6B_6 + 3B_9 = 0 \qquad \Delta E_{10}^0 = \Delta H_{10}^0 = -687.9 \text{ kJ/mol}$$

This gives the following stoichiometric matrix and energy change vector

$$\boldsymbol{\nu} = \begin{array}{ccccc} B_6 & B_7 & B_8 & B_9 & \\ -4 & 3 & 0 & 0 & \rho_8 \\ -5 & 0 & 3 & 0 & \rho_9 \\ -6 & 0 & 0 & 3 & \rho_{10} \end{array} \qquad \Delta\mathbf{E}^0 = \Delta\mathbf{H}^0 = \begin{bmatrix} -127.2 \\ -494.7 \\ -687.9 \end{bmatrix}$$

Substituting $\boldsymbol{\nu}$ and $\Delta\mathbf{E}^0$ in eq 14 and performing the matrix operations, we obtain $S_6^{\mathrm{d}} = 98.3$ kJ/mol, $S_7^{\mathrm{d}} = 55.9$ kJ/mol, $S_8^{\mathrm{d}} = -33.8$ kJ/mol, and $S_9^{\mathrm{d}} = -65.5$ kJ/mol. As can be seen, cyclopropane (B_6) and cyclobutane (B_7) are unstable whereas cyclopentane (B_8) and cyclohexane (B_9) are stable. Overall, however, the instability (strain energy) decreases in the same order.

Discussion and Concluding Remarks

It is well-known that the absolute stabilities of chemical species cannot be evaluated on the basis of purely thermochemical considerations. That is, except for the trivial case of isomeric species, the thermochemical characteristics of the species are not directly related to their stabilities. It is also well-known that the only way to evaluate the stabilities of chemical species is to employ certain stoichiometric considerations. These stoichiometric considerations are various and strongly depend up on the type of stability. So far, different types of stability of species, mainly relative stabilities, have been considered separately.

In this work, a general thermodynamic and stoichiometric theory of stability of chemical species has been proposed. More specifically, a new rigorous definition, as well as an analytical equation for the stability, has been presented that explicitly relates the thermochemical and stoichiometric characteristics of the species. The main feature of this general result is a clear interpretation of the stability. Thus, the stabilities of chemical species can be always formulated in terms of a certain class of stoichiometrically unique chemical reactions and their thermochemical characteristics. This interpretation also reveals that several types of stabilities of species may be visualized and defined. In particular, in a system comprising a given set of reference and test species one can define and evaluate the overall stabilities of the species. This type of stability is the most complete in that it takes into account all possible contributions coming from both reference and test species. The overall stabilities may be further decomposed into relative and direct stabilities. Clearly, the most useful and physically insightful type of stability is the relative stability, i.e., the stability of a given species with respect to a certain set of reference species. As shown in this work, the relative stability of species is closely related to the conventional stability. At the same time, the conventional stability, as distinct from the relative stability defined in this work, is not appropriately normalized. As a consequence, in many cases the conventional stabilities of the species are erroneous.

Appendix: Enumeration of GA RERs

The main property of the GA RERs is their stoichiometric uniqueness. This means that the GA RERs are independent of the way they are generated. Here we briefly discuss two different methods of the enumeration of GA RERs.

Most easily, the GA RERs may be enumerated starting from the group matrix **g**, eq 3. If the $q + 1$ species involved in a GA RER are $B_{i_1}, B_{i_2}, ..., B_{i_q}, B_{i_{q+1}}$, where $i_1, i_2, ..., i_q, i_{q+1}$ is a set of integers satisfying the condition $1 \le i_1 < i_2 < ... < i_q < i_{q+1} \le p$, then the general equation of a GA RER denoted by $g(B_{i_1}, B_{i_2}, ..., B_{i_q}, B_{i_{q+1}})$ is given by

$$g(B_{i_1}, B_{i_2}, ..., B_{i_q}, B_{i_{q+1}}) = \sum_{k=1}^{q+1} \nu_{ik}(g) B_{i_1} = 0 \qquad \text{(A1)}$$

where

$$\nu_{i_k}(g) = \begin{vmatrix} \epsilon_{i_1,1} & \epsilon_{i_1,2} & ... & \epsilon_{i_1,q} & 0 \\ \epsilon_{i_2,1} & \epsilon_{i_2,2} & ... & \epsilon_{i_2,q} & 0 \\ ... & ... & ... & ... & ... \\ \epsilon_{i_{k-1},1} & \epsilon_{i_{k-1},2} & ... & \epsilon_{i_{k-1},q} & 0 \\ \epsilon_{i_k,1} & \epsilon_{i_k,2} & ... & \epsilon_{i_k,q} & 1 \\ \epsilon_{i_{k+1},1} & \epsilon_{i_{k+1},2} & ... & \epsilon_{i_{k+1},q} & 0 \\ ... & ... & ... & ... & ... \\ \epsilon_{i_q,1} & \epsilon_{i_q,2} & ... & \epsilon_{i_q,q} & 0 \\ \epsilon_{i_{q+1},1} & \epsilon_{i_{q+1},2} & ... & \epsilon_{i_{q+1},q} & 0 \end{vmatrix} \qquad \text{(A2)}$$

An equivalent way to write the same equation is

$$g(B_{i_1}, B_{i_2}, ..., B_{i_q}, B_{n+1}) = \begin{vmatrix} g_{i_1,1} & g_{i_1,2} & ... & g_{i_1,q} & B_{i_1} \\ g_{i_2,1} & g_{i_2,2} & ... & g_{i_2,q} & B_{i_2} \\ ... & ... & ... & ... & ... \\ g_{i_q,1} & g_{i_q,2} & ... & g_{i_q,q} & B_{i_q} \\ g_{i_{q+1},1} & g_{i_{q+1},2} & ... & g_{i_{q+1},q} & B_{i_{q+1}} \end{vmatrix} = 0 \qquad \text{(A3)}$$

A similar equation is valid for the energy change of a GA RER

$$\Delta E(g) = \begin{vmatrix} g_{i_1,1} & g_{i_1,2} & ... & g_{i_1,q} & E_{i_1} \\ g_{i_2,1} & g_{i_2,2} & ... & g_{i_2,q} & E_{i_2} \\ ... & ... & ... & ... & ... \\ g_{i_q,1} & g_{i_q,2} & ... & g_{i_q,q} & E_{i_q} \\ g_{i_{q+1},1} & g_{i_{q+1},2} & ... & g_{i_{q+1},q} & E_{i_{q+1}} \end{vmatrix} \qquad \text{(A4)}$$

Alternatively, a complete list of GA RERs may be generated starting from an arbitrary set of m linearly independent GA reactions. Let these be

$$\begin{aligned} \rho_1 &= \nu_{11}B_1 + \nu_{12}B_2 + ... + \nu_{1p}B_p = 0 \\ \rho_2 &= \nu_{21}B_1 + \nu_{22}B_2 + ... + \nu_{2p}B_p = 0 \\ &... \\ \rho_m &= \nu_{m1}B_1 + \nu_{m2}B_2 + ... + \nu_{mp}B_p = 0 \end{aligned} \qquad \text{(A4a)}$$

Let further $i_1, i_2, ..., i_q, i_{q+1}$ and $j_1, j_2, ..., i_{m-1}$ be two ordered sets of integers satisfying the condition

$$\begin{gathered} 1 \le i_1 < i_2 < ... < i_q < i_{q+1} \le p \\ 1 \le j_1 < j_2 < ... < i_{m-1} \le p \\ \{i_1, i_2, ..., i_q, i_{q+1}\} \cup \{j_1, j_2, ..., j_{m-1}\} = \{1, 2, ..., p\} \end{gathered}$$

Then, the set of species $B_1, B_2, ..., B_p$ may be partitioned into two subsets. The first one comprises $q + 1$ species $B_{i_1}, B_{i_2}, ..., B_{i_q}, B_{i_{q+1}}$ that are involved in a GA RER whereas the second subset comprises the remaining $p - (q + 1) = m - 1$ species $B_{j_1}, B_{j_2}, ..., B_{j_{m-1}}$ that are not involved in a GA RER. Accordingly, the set of m linearly independent GA reactions eq A4, may be presented as

$$\begin{aligned} \rho_1 &= \sum_{k=1}^{q+1} \nu_{1,i_k} B_{i_k} + \sum_{h=1}^{m-1} \nu_{1,j_h} B_{j_h} = 0 \\ \rho_2 &= \sum_{k=1}^{q+1} \nu_{2,i_k} B_{i_k} + \sum_{h=1}^{m-1} \nu_{2,j_h} B_{i_h} = 0 \\ &... \\ \rho_m &= \sum_{k=1}^{q+1} \nu_{m,i_k} B_{i_k} + \sum_{h=1}^{m-1} \nu_{m,j_h} B_{j_h} = 0 \end{aligned} \qquad \text{(A5)}$$

Consider now the derivation of a RER $g'(B_{i_1}, B_{i_2}, ..., B_{i_s}, B_{i_{s+1}})$ by linearly combining the above set of m linearly independent GA reactions

$$g'(B_{i_1}, B_{i_2}, ..., B_{i_s}, B_{i_{s+1}}) = \lambda_1\rho_1 + \lambda_2\rho_2 + ... + \lambda_m\rho_m = 0 \qquad \text{(A6)}$$

Clearly, $\lambda_1, \lambda_2, ..., \lambda_m$ need to be selected so as to eliminate the species $B_{j_1}, B_{j_2}, ..., B_{j_{m-1}}$, i.e., the $m - 1$ species that are not involved in a GA RER. This procedure results in

$$g'(B_{i_1}, B_{i_2}, ..., B_{i_s}, B_{i_{s+1}}) = \begin{vmatrix} \nu_{1,j_1} & \nu_{1,j_2} & ... & \nu_{1,j_{m-1}} & \rho_1 \\ \nu_{2,j_1} & \nu_{2,j_2} & ... & \nu_{2,j_{m-1}} & \rho_2 \\ ... & ... & ... & ... & ... \\ \nu_{m,j_1} & \nu_{m,j_2} & ... & \nu_{m,j_{m-1}} & \rho_m \end{vmatrix} = 0 \qquad \text{(A7)}$$

Taking into account the explicit form of ρ_1, ρ_2, ..., ρ_m, eqA5, we further have

$$g'(\mathrm{B}_{i_1}, \mathrm{B}_{i_2}, ..., \mathrm{B}_{i_s}, \mathrm{B}_{i_{s+1}}) = \begin{vmatrix} \nu_{1,j_1} & \nu_{1,j_2} & ... & \nu_{1,j_{m\text{-}1}} & \sum_{k=1}^{q+1}\nu_{1,i_k}\mathrm{B}_{i_k} + \sum_{h=1}^{m\text{-}1}\nu_{1,j_h}\mathrm{B}_{j_1} \\ \nu_{2,j_1} & \nu_{2,j_2} & ... & \nu_{2,j_{m\text{-}1}} & \sum_{k=1}^{q+1}\nu_{2,i_k}\mathrm{B}_{i_k} + \sum_{h=1}^{m\text{-}1}\nu_{2,j_h}\mathrm{B}_{j_h} \\ ... & ... & ... & ... & ... \\ \nu_{m,j_1} & \nu_{m,j_2} & ... & \nu_{m,j_{m\text{-}1}} & \sum_{k=1}^{q+1}\nu_{m,i_k}\mathrm{B}_{i_k} + \sum_{h=1}^{m\text{-}1}\nu_{m,j_h}\mathrm{B}_{j_h} \end{vmatrix}$$

$$= \sum_{k=1}^{q+1} \begin{vmatrix} \nu_{1,j_1} & \nu_{1,j_2} & ... & \nu_{1,j_{m\text{-}1}} & \nu_{1,i_k} \\ \nu_{2,j_1} & \nu_{2,j_2} & ... & \nu_{2,j_{m\text{-}1}} & \nu_{2,i_k} \\ ... & ... & ... & ... & ... \\ \nu_{m,j_1} & \nu_{m,j_2} & ... & \nu_{m,j_{m\text{-}1}} & \nu_{m,i_k} \end{vmatrix} \mathrm{B}_{i_k} +$$

$$\sum_{h=1}^{m\text{-}1} \begin{vmatrix} \nu_{1,j_1} & \nu_{1,j_2} & ... & \nu_{1,j_{m\text{-}1}} & \nu_{1,j_h} \\ \nu_{2,j_1} & \nu_{2,j_2} & ... & \nu_{2,j_{m\text{-}1}} & \nu_{2,j_h} \\ ... & ... & ... & ... & ... \\ \nu_{m,j_1} & \nu_{m,j_2} & ... & \nu_{m,j_{m\text{-}1}} & \nu_{m,j_h} \end{vmatrix} \mathrm{B}_{j_h} = 0$$

It is seen that whenever $h = 1$, $h = 2$, ..., $h = m - 1$ two columns in the second determinant are equal and, consequently, the determinant is equal to zero. That is, the stoichiometric coefficients of the species B_{j_1}, B_{j_2}, ..., $\mathrm{B}_{j_{m-1}}$ are equal to zero, i.e., are not involved in the resulting GA RER. Hence, the equation of the GA RER $g'(\mathrm{B}_{i_1}, \mathrm{B}_{i_2}, ..., \mathrm{B}_{i_s}, \mathrm{B}_{i_{s+1}})$ is

$$g'(\mathrm{B}_{i_1}, \mathrm{B}_{i_2}, ..., \mathrm{B}_{i_s}, \mathrm{B}_{i_{s+1}}) = \sum_{k=1}^{q+1} \nu'_{i_k}(g)\mathrm{B}_{i_k} = 0 \qquad \text{(A8)}$$

where

$$\nu'_{i_k}(g) = \begin{vmatrix} \nu_{1,j_1} & \nu_{1,j_2} & ... & \nu_{1,j_{m\text{-}1}} & \nu_{1,i_k} \\ \nu_{2,j_1} & \nu_{2,j_2} & ... & \nu_{2,j_{m\text{-}1}} & \nu_{2,i_k} \\ ... & ... & ... & ... & ... \\ \nu_{m,j_1} & \nu_{m,j_2} & ... & \nu_{m,j_{m\text{-}1}} & \nu_{m,i_k} \end{vmatrix} \qquad \text{(A9)}$$

Obviously, the thermodynamic functions of the GA RERs may be expressed through the thermodynamic functions of the linearly independent GA reactions ρ_1, ρ_2, ..., ρ_m via similar relations, i.e.,

$$\Delta E'(g) = \begin{vmatrix} \nu_{1,j_1} & \nu_{1,j_2} & ... & \nu_{1,j_{m\text{-}1}} & \Delta E_1 \\ \nu_{2,j_1} & \nu_{2,j_2} & ... & \nu_{2,j_{m\text{-}1}} & \Delta E_2 \\ ... & ... & ... & ... & ... \\ \nu_{m,j_1} & \nu_{m,j_2} & ... & \nu_{m,j_{m\text{-}1}} & \Delta E_m \end{vmatrix} \qquad \text{(A10)}$$

The stoichiometric uniqueness of the GA RERs implies that

$$g'(\mathrm{B}_{i_1}, \mathrm{B}_{i_2}, ..., \mathrm{B}_{i_s}, \mathrm{B}_{i_{s+1}}) = \gamma g(\mathrm{B}_{i_1}, \mathrm{B}_{i_2}, ..., \mathrm{B}_{i_s}, \mathrm{B}_{i_{s+1}}) \qquad \text{(A11)}$$

where γ is a constant.

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