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Theoretical Study on Thermodynamic Properties of C_1-C_{16} Alkanes: A 3-Parameter Least-Squared Calibration

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The hybrid density-functional theory (DFT) calculated energies of C_1-C_{16} straight-chain alkanes were obtained based on B3LYP/6-311++G(3df,2pd) single-point energies and the related thermal corrections of B3LYP/6-31G(d,p) optimized geometries. A 3-parameter modification equation and the least-squares approach are adopted to calibrate all the molecular calculated energies to produce accurate enthalpies of formation (ΔH_f) and Gibbs free energies of formation (ΔG_f), respectively. This study found that all compounds had 0.04% average relative error (A.R.E.) for the atomization energies, with a mean value of absolute error (M.A.E.) of just 1.1 kJ/mol for the ΔH_f and 1.9 kJ/mol for the ΔG_f of formation. The ΔH_f values obtained in this work are superior to the improved G3(MP2)//B3LYP calculations for the same 16 alkanes in pertinent literature.

1. Introduction

The thermodynamic properties of molecules are important in thermochemistry and chemical equilibrium. Especially the formation enthalpy is used to realize reaction heat, and the Gibbs energy is used to determine reaction spontaneity. How to obtain accurate data for use recently has become a public issue. Studies on quantum chemical calculations have produced lower calculation errors than those in experiments, and were found to use calibration based on Gaussian-1 theory,[1,2] G2 theory,[3,4] G3 theory,[5−8] G3X theory,[9,10] and other methods.[11−15]

This study presents a simple means of obtaining better formation enthalpies and Gibbs free energies of formation of C_1-C_{16} straight-chain alkanes. A 3-parameter modification equation was established and the least-squares approach was used for the calculation work. The atomic energies of the C and H atoms were modified mainly because differences in atom number influence the calculation of the related energies. In a manner related to the concept of size consistency, i.e., that relative errors in a calculation should increase more or less proportionally to the size (or number of atoms) of the molecule, a molecule with many atoms requires better correction than one with a few atoms to yield reasonable results for computational energy. Moreover, the parameters obtained by using the least-squares method can be extended to accurately forecast the related energies (either unknown or unpublished) of enormous molecules with the same C−H series.

2. Calculations

2.1. Geometric Optimization and Molecular Energy Calculation. A composite method from the Gaussian 98 program (G98),[16] namely the B3LYP/6-311++G(3df,2pd)//B3LYP/6-31G(d,p) two-step type calculation, was used to obtain the related molecular energies. On the basis of canonical ensemble type formulation, the internal energy U is expressed as

$$U = E_{\mathrm{ele}} + E_{\mathrm{thermal}} \qquad (E_{\mathrm{ele}} \gg E_{\mathrm{thermal}}) \qquad (1)$$

In eq 1, the thermal energy part (E_{thermal}) includes vibrational energy, classical translational, and rotational energies. The enthalpy (H) and Gibbs free energy (G) are defined in eqs 2 and 3.

$$H = U + PV = U + RT \qquad (\text{for ideal gas } PV = RT) \qquad (2)$$

$$G = H - TS \qquad (3)$$

The E_{thermal} in eq 1 and entropy (S) in eq 3 heavily depend on the accuracy of molecular geometry and vibration frequencies. In the optimization and vibration calculations, the B3LYP type[17,18] with 6-31G(d,p) basis is adequate for performing related work to obtain reliable geometry and vibration frequencies. Rather than Moller−Plesset perturbation (MP2) or other ab initio with the same 6-31G(d,p) basis methods, the B3LYP/6-31G(d,p) method chosen herein primarily owing to its scaling factor[19] for vibration frequency approaches 1.0 (generally ranging between 0.98 and 1.0 and with barely any apparent difference from the experimental vibration frequency). Based on the precise calculation of vibrational frequencies, both E_{thermal} and S resulting from the statistical thermodynamic calculation are more reliable. Subsequently, a larger triple-ζ polarized function and diffused basis included, or B3LYP/6-311++G(3df,2pd), method was used to correlate with the requirements for intergrated electron correlation energy calculation to obtain an accurate electronic energy (E_{ele}) for our study of molecules and atoms.

Molecular thermal enthalpy and Gibbs energy were determined by adding a thermal correction (from B3LYP/6-31G(d,p) output) to the B3LYP/6-311++G(3df,2pd) calculated single-point molecular energy.

2.2. Least-Squares Approach To Calibrate ΔH_f and ΔG_f. This part of the calculation first determines the energy of atomization ($\Delta H_{a,\mathrm{cal}}$ and $\Delta G_{a,\mathrm{cal}}$) for a specific $C_{n_C}H_{n_H}$ molecule (eq 4) by DFT data and then establishes a 3-parameter equation auxiliarily to calibrate the least-squares energy of atomization ($\Delta H_{a,\mathrm{ls}}$ and $\Delta G_{a,\mathrm{ls}}$). All types of energy are compared to the experimental energies of atomization ($\Delta H_{a,\mathrm{obs}}$ and $\Delta G_{a,\mathrm{obs}}$), and finally experimental values are introduced to obtain the enthalpy

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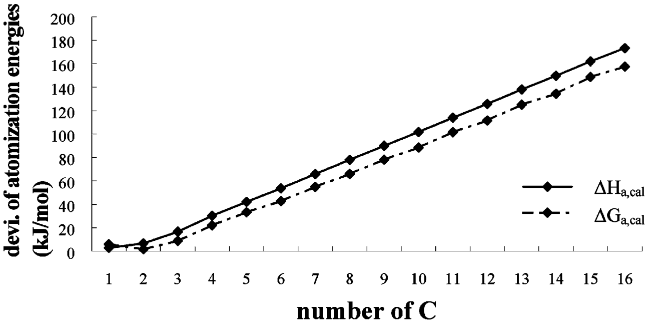

Figure 1. The deviation of calculated atomization energies for C_1-C_{16} alkanes by the hybrid DFT method.

TABLE 1: Comparison of the Enthalpies of Atomization of C_1-C_{16} Alkanes at 298 K

	energy[a]			
compd	H_{cal}[b]	$\Delta H_{a,obs}$[c]	$\Delta H_{a,cal}$(R.E.)[d]	$\Delta H_{a,ls}$(R.E.)[d]
CH_4	−40.4871	1663.39	1660.47(−0.18)	1656.46(−0.42)
C_2H_6	−79.7834	2825.83	2819.17(−0.24)	2826.95(0.04)
n-C_3H_8	−119.0808	3997.62	3980.94(−0.42)	4000.51(0.07)
n-C_4H_{10}	−158.3780	5172.53	5142.32(−0.58)	5173.68(0.02)
n-C_5H_{12}	−197.6752	6345.43	6303.41(−0.66)	6346.56(0.02)
n-C_6H_{14}	−236.9725	7518.79	7465.02(−0.72)	7519.97(0.02)
n-C_7H_{16}	−276.2697	8691.99	8626.17(−0.76)	8692.92(0.01)
n-C_8H_{18}	−315.5668	9865.28	9787.24(−0.79)	9865.78(0.01)
n-C_9H_{20}	−354.8640	11038.47	10948.52(−0.81)	11038.85(0.00)
n-$C_{10}H_{22}$	−394.1613	12211.71	12109.93(−0.83)	12212.05(−0.00)
n-$C_{11}H_{24}$	−433.4584	13384.95	13270.90(−0.85)	13384.82(−0.00)
n-$C_{12}H_{26}$	−472.7557	14558.14	14432.38(−0.86)	14558.09(−0.00)
n-$C_{13}H_{28}$	−512.0528	15731.39	15593.35(−0.88)	15730.85(−0.00)
n-$C_{14}H_{30}$	−551.3501	16904.63	16754.89(−0.89)	16904.18(−0.00)
n-$C_{15}H_{32}$	−590.6471	18077.86	17915.79(−0.90)	18076.88(−0.01)
n-$C_{16}H_{34}$	−629.9446	19251.17	19077.74(−0.90)	19250.62(−0.00)
A.|R.E.|	–	–	0.70%	0.04%

[a] H_{cal} in au, other values in kJ/mol. [b] B3LYP/6-311++G(3df,2pd)//B3LYP/6-31G(d,p) calculation results; H_{cal} is −37.855111 au for C and −0.499897 au for H. [c] $\Delta H_{f,obs}$ is 716.68 kJ/mol for C and 217.97 kJ/mol for H. [d] R.E. is given in % in parentheses.

($\Delta H_{f,ls}$) and Gibbs energy of formation ($\Delta G_{f,ls}$) of a target molecule (eqs 5 and 6)

$$C_{n_C}H_{n_H}(g) \rightarrow n_C C(g) + n_H H(g) \quad (4)$$

$$\Delta H_f(C_{n_C}H_{n_H},gas)_{ls} = n_C \Delta H_f(C_{gas})_{obs} + n_H \Delta H_f(H_{gas})_{obs} - \Delta H_{a,ls} \quad (5)$$

$$\Delta G_f(C_{n_C}H_{n_H},gas)_{ls} = n_C \Delta G_f(C_{gas})_{obs} + n_H \Delta G_f(H_{gas})_{obs} - \Delta G_{a,ls} \quad (6)$$

where n_C and n_H are the number of C and H atoms, respectively.

3. Results and Discussion

This investigation modeled C_1-C_{16} alkanes as stable molecules (Figure 1) with real positive vibration frequencies. Tables 1−4 list the thermodynamic energies of the molecules for comparison.

3.1. Program-Calculated Energies. B3LYP/6-31G(d,p)-calculated thermal corrections to enthalpy and Gibbs energy were added to B3LYP/6-311++G(3df,2pd) SCF molecular energy to obtain the related H_{cal} and G_{cal} of the target molecules and their corresponding composite atoms, as listed in Tables 1 and 2. Regarding the atomization reaction of a $C_{n_C}H_{n_H}$ molecule (eq 1), the atomization energies ($\Delta H_{a,cal}$ and $\Delta G_{a,cal}$) were calculated by using eqs 7 and 8, and Tables 1 and 2 list the comparison results. For the 16 listed alkanes, the average relative errors of atomization energy between the calculations and observations are only approximately 0.70%. This method is essentially reliable and accordingly is used for further calculations. From Figure 1, the calculated atomization energy errors monotonically increased with increasing carbon numbers or molecular size.

TABLE 2: Comparison of the Gibbs Energies of Atomization of C_1-C_{16} Alkanes at 298 K

	energy[a]			
compd	G_{cal}[b]	$\Delta G_{a,obs}$[c]	$\Delta G_{a,cal}$(R.E.)[d]	$\Delta G_{a,ls}$(R.E.)[d]
CH_4	−40.5106	1535.09	1541.05(0.39)	1532.69(−0.16)
C_2H_6	−79.8092	2594.93	2593.22(−0.07)	2595.81(0.03)
n-C_3H_8	−119.1113	3663.22	3654.46(−0.24)	3668.02(0.13)
n-C_4H_{10}	−158.4121	4734.65	4712.59(−0.47)	4737.11(0.05)
n-C_5H_{12}	−197.7128	5803.62	5770.28(−0.57)	5805.75(0.04)
n-C_6H_{14}	−237.0145	6873.25	6830.54(−0.62)	6876.97(0.05)
n-C_7H_{16}	−276.3150	7942.76	7887.91(−0.69)	7945.30(0.03)
n-C_8H_{18}	−315.6159	9012.10	8946.13(−0.73)	9014.48(0.03)
n-C_9H_{20}	−354.9164	10081.44	10003.25(−0.78)	10082.56(0.01)
n-$C_{10}H_{22}$	−394.2176	11150.78	11062.28(−0.79)	11152.55(0.02)
n-$C_{11}H_{24}$	−433.5177	12220.17	12118.48(−0.83)	12219.71(−0.00)
n-$C_{12}H_{26}$	−472.8191	13289.47	13177.86(−0.84)	13290.04(0.00)
n-$C_{13}H_{28}$	−512.1191	14358.81	14233.68(−0.87)	14356.82(−0.01)
n-$C_{14}H_{30}$	−551.4207	15428.19	15293.81(−0.87)	15427.91(−0.00)
n-$C_{15}H_{32}$	−590.7203	16497.53	16348.80(−0.90)	16493.86(−0.02)
n-$C_{16}H_{34}$	−630.0221	17566.83	17409.18(−0.90)	17565.19(−0.01)
A.|R.E.|, %			0.66	0.04

[a] G_{cal} in au, other values in kJ/mol. [b] B3LYP/6-311++G(3df,2pd)//B3LYP/6-31G(d,p) calculation results; G_{cal} is −37.872017 au for C and −0.512911 au for H. [c] $\Delta G_{f,obs}$ is 671.26 kJ/mol for C and 203.25 kJ/mol for H. [d] R.E. is given in % in parentheses.

TABLE 3: Comparison of the Enthalpies of Formation of C_1-C_{16} Alkanes at 298 K

	energy[a]			
compd	$\Delta H_{f,obs}$[b]	$\Delta H_{f,cal}$(A.E.)	$\Delta H_{f,ls}$(A.E.)	$\Delta H_{f,G3}$[c](A.E.)
CH_4	−74.9	−71.9(2.9)	−68.0(6.9)	−73.7(1.2)
C_2H_6	−84.7	−78.0(6.7)	−85.8(−1.1)	−83.1(1.6)
n-C_3H_8	−103.9	−87.2(16.7)	−106.8(−2.9)	−103.8(0.1)
n-C_4H_{10}	−126.2	−95.5(30.2)	−127.4(−1.2)	−125.1(1.1)
n-C_5H_{12}	−146.4	−104.4(42.0)	−147.5(−1.1)	−146.1(0.3)
n-C_6H_{14}	−167.2	−113.4(53.8)	−168.4(−1.2)	−167.3(−0.1)
n-C_7H_{16}	−187.8	−122.0(65.8)	−188.7(−0.9)	−188.3(−0.5)
n-C_8H_{18}	−208.5	−130.4(78.0)	−209.0(−0.5)	−209.6(−1.1)
n-C_9H_{20}	−229.0	−139.1(90.0)	−229.4(−0.4)	−230.8(−1.8)
n-$C_{10}H_{22}$	−249.7	−147.9(101.8)	−250.0(−0.3)	−252.0(−2.3)
n-$C_{11}H_{24}$	−270.3	−156.2(114.1)	−270.2(0.1)	−273.2(−2.9)
n-$C_{12}H_{26}$	−290.9	−165.1(125.8)	−290.8(0.1)	−294.4(−3.5)
n-$C_{13}H_{28}$	−311.5	−173.5(138.0)	−311.0(0.5)	−315.6(−4.1)
n-$C_{14}H_{30}$	−332.1	−182.4(149.7)	−331.7(0.4)	−336.8(−4.7)
n-$C_{15}H_{32}$	−352.8	−190.7(162.1)	−351.8(1.0)	−358.0(−5.2)
n-$C_{16}H_{34}$	−373.5	−200.0(173.4)	−372.9(0.6)	−379.2(−5.7)
M.|A.E.|		81.2	1.1	2.3

[a] All in kJ/mol. [b] Taken from ref 20, Tables 8 and 9, pp 131−159. [c] See ref 8.

$$\Delta H_{a,cal} = n_C H(C_{gas})_{cal} + n_H H(H_{gas})_{cal} - H(C_{n_C}H_{n_N},gas)_{cal} \quad (7)$$

$$\Delta G_{a,cal} = n_C G(C_{gas})_{cal} + n_H G(H_{gas})_{cal} - G(C_{n_C}H_{n_H},gas)_{cal} \quad (8)$$

The $\Delta H_{f,cal}$ and $\Delta G_{f,cal}$ were obtained when the experimental $\Delta H_{f,obs}$ and $\Delta G_{f,obs}$ of C, H atoms[20] and $\Delta H_{a,cal}$ and $\Delta G_{a,cal}$ of molecules were included in the calculation. Tables 3 and 4 list the mean value of absolute error (M.A.E.) as 81.2 kJ/mol for enthalpy of formation and as 70.4 kJ/mol for Gibbs energy of formation, and allow comparison with the experimental $\Delta H_{f,obs}$ and $\Delta G_{f,obs}$ values.[20]

TABLE 4: Comparison of the Gibbs Energies of Formation of C_1-C_{16} Alkanes at 298 K

	energy[a]		
compd	$\Delta G_{f,obs}$[b]	$\Delta G_{f,cal}$(A.E.)	$\Delta G_{f,ls}$(A.E.)
CH_4	−50.8	−56.8(−6.0)	−48.4(2.4)
C_2H_6	−32.9	−31.2(1.7)	−33.8(−0.9)
n-C_3H_8	−23.5	−14.7(8.8)	−28.3(−4.8)
n-C_4H_{10}	−17.2	4.9(22.1)	−19.6(−2.5)
n-C_5H_{12}	−8.4	25.0(33.4)	−10.5(−2.1)
n-C_6H_{14}	−0.3	42.5(42.8)	−4.0(−3.7)
n-C_7H_{16}	8.0	62.8(54.8)	5.5(−2.5)
n-C_8H_{18}	16.4	82.4(66.0)	14.0(−2.4)
n-C_9H_{20}	24.8	103.0(78.2)	23.7(−1.1)
n-$C_{10}H_{22}$	33.2	121.7(88.5)	31.5(−1.7)
n-$C_{11}H_{24}$	41.6	143.3(101.7)	42.1(0.5)
n-$C_{12}H_{26}$	50.0	161.7(111.7)	49.5(−0.5)
n-$C_{13}H_{28}$	58.5	183.6(125.1)	60.4(1.9)
n-$C_{14}H_{30}$	66.8	201.2(134.4)	67.1(0.3)
n-$C_{15}H_{32}$	75.2	224.0(148.8)	78.9(3.7)
n-$C_{16}H_{34}$	83.7	241.3(157.6)	85.3(1.6)
M.|A.E.|		70.4	1.9

[a] All in kJ/mol. [b] Calculated with $\Delta H_{f,obs}$ and S_{obs} obtained from ref 2, $\Delta G_{f,obs} = \Delta H_{f,obs} - T\Delta S_{obs}$, at 298 K.

TABLE 5: Calibration Parameters of the Least-Squares Estimation Equations

parameter[a]	calibration of ΔH_f	calibration of ΔG_f
A	−27.40124	−22.43968
B	8.61127	13.83654
C	2.99261	0.73463

[a] A is given in kJ mol^{-1}; B and C are given in kJ mol^{-1} atom^{-1}.

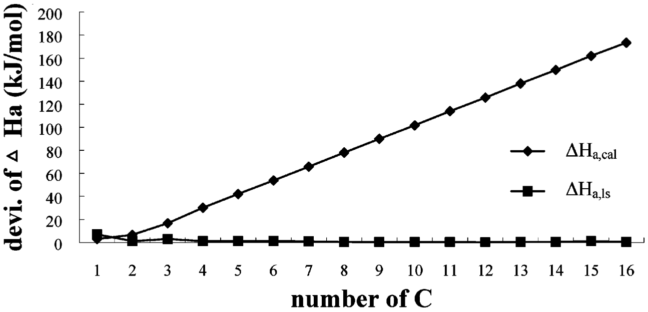

Figure 2. Comparison of the deviation of calculated and calibrated ΔH_a for C_1-C_{16} alkanes.

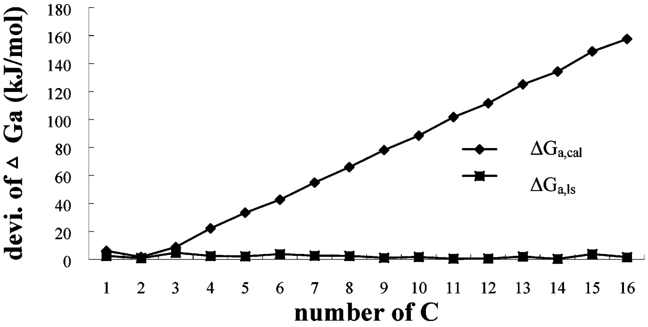

Figure 3. Comparison of the deviation of calculated and calibrated ΔG_a for C_1-C_{16} alkanes.

3.2. Least-Squares Modified Energies. Owing to the results of $\Delta H_{f,cal}$ and $\Delta G_{f,cal}$ containing obvious errors and being difficult to use, this work attempts to create a polymetric modification equation, based on a least-squares estimation, to reduce the related energy errors. The number of each species of atom in a specific alkane molecule containing C and H atoms influences the calculated energies. Two 3-parameter equations were created (eqs 9 and 10) in which parameter A_h (or A_g) is a constant item and B_h and C_h (or B_g and C_g) are modified according to the number of C and H atoms. Simply for a satisfactory requirement for a size-consistent idea,[21,22] the modified computation focuses on molecular sizes and on the number of different atoms in an alkane compound in this study.

$$\Delta H_{a,ls} = \Delta H_{a,cal} + A_h + B_h n_{C_i} + C_h n_{H_i} \tag{9}$$

$$\Delta G_{a,ls} = \Delta G_{a,cal} + A_g + B_g n_{C_i} + C_g n_{H_i} \tag{10}$$

where n_{C_i} and n_{H_i} are the number of C and H atoms of the ith molecule

Since C_1-C_{16} alkanes with known experimental ΔH_f and ΔG_f in Tables 3 and 4 were selected for further study, the square summation of the atomization energy error between the least-squares modified values and the experimental values was noted to resemble that in eqs 11 and 12.

$$\epsilon_{r_H} = \sum_{i=1}^{17} (\Delta H_{ai,obs} - \Delta H_{ai,ls})^2 = \sum_{i=1}^{17} (\Delta H_{ai,obs} - \Delta H_{ai,cal} - A_h - B_h n_{C_i} - C_h n_{H_i})^2 \tag{11}$$

$$\epsilon_{r_G} = \sum_{i=1}^{17} (\Delta G_{ai,obs} - \Delta G_{ai,ls})^2 = \sum_{i=1}^{17} (\Delta G_{ai,obs} - \Delta G_{ai,cal} - A_g - B_g n_{C_i} - C_g n_{H_i})^2 \tag{12}$$

At this point an additional 17th molecule (benzene) is supplied, and the first derivative of ϵ_{r_H} (or ϵ_{r_G}) with respect to A_h, B_h, and C_h (or A_g, B_g, and C_g) is allowed to equal zero, after which the simultaneous equations are solved nonlinearly (or linear dependency in solving the secular determinant is avoided) using extra data on benzene (M.A.E. in ΔH_f and ΔG_f are both 0.0 kJ/mol) to obtain the values of A_h, B_h, and C_h (or A_g, B_g, and C_g). Table 5 lists the computational results.

According to the least-squares modified $\Delta H_{a,ls}$ and $\Delta G_{a,ls}$ results, the average relative errors of atomization energies reduced to 0.04%, superior to the results of the direct program calculated output (Tables 1 and 2 and Figures 2 and 3). Furthermore, the $\Delta H_{f,ls}$ and $\Delta G_{f,ls}$ were calculated based on the above $\Delta H_{a,ls}$ and $\Delta G_{a,ls}$, using eqs 2 and 3. The mean absolute value of absolute error was just 1.1 kJ/mol for the enthalpy of formation, significantly better than the G3(MP2)//B3LYP calculation results obtained by Redfern et al., resulting in 2.3 kJ/mol of error.[8] Similarly, the mean absolute value of absolute error is 1.9 kJ/mol for Gibbs energy of formation (Tables 3 and 4).

4. Conclusion

This investigation initially calculated the atomization energy for C_1-C_{16} alkanes by using the hybrid DFT B3LYP/6-311++G(3df,2pd)//B3LYP/6-31G(d,p) method, and then calibrated the obtained atomization energy by using a 3-parameter modification equation. The modified approach achieves markedly better results than direct program calculated output, with a average relative error for $\Delta H_{a,cal}$ to $\Delta H_{a,ls}$ improving from 0.70% to 0.04%, while that for $\Delta G_{a,cal}$ to $\Delta G_{a,ls}$ improves from 0.66% to 0.04%. These analytical results are sufficiently encouraging to justify further calculation work. Consequently, this study calibrates the thermodynamic properties of the selected 16 alkanes such as enthalpy of formation and Gibbs energy of formation and identifies the mean value of absolute error at around 1.1−1.9 kJ/mol for the least-squares estimation and exhibits a more significant improvement than the errors of several tens of kJ/mol from the directly calculated program outputs. These calculation results confirm that the least-squares approach derived polyparameter modification equation can effectively and reliably calculate the ΔH_f and ΔG_f of the alkane series molecules. Conversely, the most recently improved Gaussian 3 theory calculation comprises complicated calculation methods that are effective, but has a limited computational memory space to calibrate the molecular formation enthalpies directly for an alkane that contains over eight carbon numbers.[8] In addition to conserving large quantities of computational time, the least-squares calibration method can calculate large alkane species that contain 16 above C's all by using the identical computational procedure. Given our belief that this approach can be extended to derive 4-parameter modification equations[23] to calibrate the C, H, and N and C, H, and O three-element compounds, as well as deriving a 5-parameter modification equation[23,24] to calibrate the C, H, N, and O four-element compounds, the obtained parameters ultimately can be employed to forecast the corresponding energies of ΔH_f and ΔG_f of complicated organic compounds.

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