Efficient ab initio Estimation of Formation Enthalpies for Organic Compounds: Extension to Sulfur and Critical Evaluation of Experimental Data

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Abstract

The efficient protocol for estimation of gas-phase enthalpies of formation developed previously for C, H, O, N, and F elements was extended to sulfur. The protocol is based on local coupled-cluster with single, double, and perturbative triple excitations (CCSD(T)) approximation and allows rapid evaluation of compounds with sizes computationally prohibitive to canonical CCSD(T) using quadruple-zeta basis sets. As a part of model development, a comprehensive review and critical evaluation of experimental data was performed for 87 sulfur-containing organic and inorganic compounds. A compact model with only three empirical parameters for sulfur introduced to address the effects beyond frozen-core CCSD(T) was developed. The model exhibits about 2 kJ·mol^{-1} standard deviation over a set of experimental values for a diverse collection of sulfur-containing compounds. The complete basis set version of the model demonstrates a similar performance and requires only one empirical parameter. Multiple problems with the existing experimental data were identified and discussed. In addition, a lack of reliable data for certain important classes of sulfur compounds was found to impede the model generalization and confident performance assessment.

Introduction

Enthalpy of formation represents an important thermochemical property with numerous practical applications.[1] As such, its efficient and accurate estimation is of great interest for process modeling and design,[2] as well as for validation of existing and newly produced experimental data.[3] *Ab initio* methods have become an essential resource for prediction of enthalpies of formation;[4] yet, until recently, the theory levels required to achieve the accuracy needed by applications were computationally prohibitive for large-scale and routine processing of compounds of practical interest, especially in terms of size. However, with recent availability of local coupled-cluster methods[5–13] accelerated with the "resolution of identity" (density fitting) procedures,[14–16] accurate approximations of coupled-cluster with

single, double, and perturbative triple excitations (CCSD(T)) approach became practical even for moderate computational resources. With these methods, a medium-sized compound can be processed in a matter of a few hours.[8,17,18]

In our previous work, we developed a protocol based on local CCSD(T) that allows ideal-gas $\Delta_\mathrm{f}H^\circ$ estimation for closed-shell compounds composed of C, H, O, or N atoms with the accuracy competitive with that of a typical experiment.[17,18] Later, this protocol was extended to include fluorine.[19] Within this approach, ideal-gas enthalpy of formation is estimated as

$$\Delta_\mathrm{f}H^\circ = E + \mathrm{ZPVE} + \Delta_0^T H - \sum_{\mathrm{types}} n_i h_i, \tag{1}$$

where E is the total electronic energy, ZPVE is the zero-point vibrational energy, and $\Delta_0^T H$ is the thermal correction from (0 to 298.15) K. The summation in the last term of Eq. 1 is performed over all atomic types present in the compound; n_i is the ith type count, and h_i is the type-specific constant. Mathematically, Eq. 1 is equivalent to determination of $\Delta_\mathrm{f}H^\circ$ from atomization energy and h_i can be formally defined using computed atomic electronic energies, reference enthalpies of formation, and reference enthalpy changes for individual atomic species. Direct use of atomic species as references is problematic, both in terms of implementation within the local coupled-cluster framework and the overall level of theory required for accurate description. For example, Klippenstein et al. recently suggested the use of molecular reference species instead.[20] Here, we determine h_i empirically, similar to earlier atom-equivalent proposals,[21,22] by fitting to thoroughly vetted experimental data. Once the effective atomic type enthalpies are established, the protocol does not require any auxiliary experimental data as in the approaches based on enthalpies of reactions,[23] while approximating the enthalpies of reactions of compound in question and the compounds from the data set used to determine h_i. Additional benefit of this semi-empirical approach is the flexibility to account for the effects beyond frozen-core local CCSD(T) by introducing different atomic types for the same element (based, *e.g.*, on its bonding patterns) given the theoretical or statistical justification. Previously, we used two different types for carbon[18]

as was necessitated by the statistical analysis of experimental data.

The success of the approach based on Eq. 1, to a large extent, rests on the quality of the experimental data used to obtain h_i, and their critical evaluation represents an essential and vital part of the model development. For the CHON-compounds,[17,18] each data point in the diverse data set used for the parameterization of the method had multiple and consistent experimental verifications. This was not the case for fluorinated organics when only limited amount of data was available with multiple experimental problems identified.[19] As a result, the uncertainties of predictions were higher as compared to those for the CHON systems, even after exhaustive critical evaluation of the original experimental sources.

In this work, we extend the protocol to a third-row element, sulfur. This poses a number of challenges. First, the issue of the experimental data needs to be addressed. The experimental enthalpies of formation for CHON molecules are normally determined from combustion experiments in a static bomb,[24] while the measurements for S-containing compounds require a rotating-bomb calorimeter. This technique have been used only by a few groups. Thus, the experimental $\Delta_{\mathrm{f}}H^{\circ}$ values are only available for less than 400 sulfur-containing compounds as compared to several thousands for CHON compounds. These experiments are extremely time- and resource-consuming, and, consequently, are almost never independently verified. In other words, "a single measurement from a single research group" represents the vast majority of the existing data. Second, there are also theoretical challenges. In contrast to the previously considered elements, sulfur has low-lying d-orbitals available to hybridization and exhibits multiple accessible oxidation states.[25] Limited high-level theory analysis for compounds with S in high oxidation states (*i.e.*, SO_2 and SO_3) suggests that the contributions beyond frozen-core CCSD(T) (*e.g.*, scalar relativistic and spin-orbital corrections) differ substantially from those with S(II).[26,27] For example, the reported scalar relativistic corrections to atomization energy for H_2O, H_2S, SO_2, and SO_3 are -1.1, -1.6, -3.3, and -7.4 kJ·mol^{-1}, respectively.[27]

It is, therefore, expected that the protocol described by Eq. 1 would require multiple

atomic types or other corrections to describe S-containing compounds with target accuracy. Compounds with S in high oxidation states were also shown to present difficulties for popular budget composite methods.[28] In the following, we address the challenges outlined above. We conduct a comprehensive critical analysis of the available experimental data and generate the data set for parametrization of Eq. 1 for S-containing closed-shell compounds. As a result, we produce a compact semi-empirical parameterization for sulfur that is consistent with our previous work on CHONF systems,[17–19] i.e., without resorting to explicit introduction of *ab initio*-based corrections beyond frozen-core CCSD(T).

Computational Details

The computations followed the **aLL5** protocol from Ref. 18 that was found to be a reasonable compromise between the accuracy and the computational cost on a typical multi-core computer system. A brief description of the protocol follows; for further details, the reader is referred to the original publication.[18] The initial optimization and computation of vibrational frequencies were performed at B3LYP-D3(BJ)/def2-TZVP level. Separate vibrational frequency scaling factors were used for calculation of zero-point vibrational energies (ZPVE) and thermal correction to the enthalpy, $\Delta_0^T H$. For ZPVE, a single scaling factor of 0.990 was used. For rigid rotor/harmonic oscillator-approximated $\Delta_0^T H$, factors of 0.960 and 0.985 were applied to hydrogen stretches and all other modes, respectively. The geometries used for local coupled-cluster calculations were optimized with the density-fitted (resolution-of-identity) second-order Møller-Plesset perturbation theory (DF-MP2). The single-point energy calculations were performed with the 2016 version of LCCSD(T) of Kállay et al.[11,12] In both calculations, aug-cc-pVQZ basis set was used for all atoms, except sulfur. For sulfur, we utilized aug-cc-pV(Q+d)Z,[29] a revised version augmented with tight d-functions to address core polarization effects for third-row atoms.[30,31] DFT calculations were performed with Gaussian 16,[32] DF-MP2 was done with Psi4 v1.3.2,[33,34] and LCCSD(T) was carried out

with MRCC (release of February 9, 2019).[35,36] All correlated calculations used frozen-core approximation.

For LCCSD(T) extrapolation to complete basis set (CBS), additional LCCSD(T) computations were carried out with quintuple-zeta basis sets, aug-cc-pV(5+d)Z for sulfur and aug-cc-pV5Z for other atoms. For each molecule, these computations were performed only for the conformer with the lowest LCCSD(T) energy obtained with the quadruple-zeta basis set. The SCF energy contribution was extrapolated using the Karton-Martin modification[37] of Jensen's extrapolation formula:[38]

$$E_{\infty}^{\mathrm{SCF}} = E^{\mathrm{SCF}}(L) + \frac{E^{\mathrm{SCF}}(L) - E^{\mathrm{SCF}}(L-1)}{c_1 - 1} \tag{2}$$

where

$$c_1 = \frac{L}{L+1} \exp\left(9\left(\sqrt{L} - \sqrt{L-1}\right)\right) \tag{3}$$

and $L = 5$.

The CCSD(T) correlation energy contribution was extrapolated with the equation

$$E_{\infty}^{\mathrm{corr}} = E^{\mathrm{corr}}(L) + \frac{E^{\mathrm{corr}}(L) - E^{\mathrm{corr}}(L-1)}{\left(\frac{L}{L-1}\right)^3 - 1} \tag{4}$$

which, to a large extent, is based on empirical observations (see, *e.g.*, Ref. 39).

As discussed below, additional corrections were evaluated for two selected cases, dimethyl sulfoxide and dimethyl sulfone. The core-valence contributions to atomization energies were computed at the canonical CCSD(T)/aug-cc-pwQZ theory level. The scalar relativistic contributions were found from the differences between the non-relativistic CCSD(T)/aug-cc-pVQZ and the second-order Douglas-Kroll-Hess[40,41] CCSD(T)/aug-cc-pVQZ-DK calculations. These calculations were also performed with Psi4. The computations for atoms were conducted using UHF determinants, while atomic spin-orbit coupling energies were calculated using atomic energy levels.

Previously, our CHON training data set was chosen to minimize the conformational contributions to the resulting $\Delta_f H^\circ$.[17] Here, due to the insufficient amount of experimental data for rigid molecules, those with multiple conformations had to be considered. As previously,[18,19] to account for multiple conformations, we adopted the model that assumes the ideal-gas equilibrium mixture of individual conformers with the entropy component of the standard Gibbs energy computed using the same rigid rotor/harmonic oscillator approximation as was used for $\Delta_0^T H$ terms. Enthalpy of formation for a given compound was computed as the Gibbs-energy average for the conformer population.

The following CHNOF parameters in Eq. 1 established previously[18,19] were fixed: h(C saturated or aromatic) = –99910.32 kJ·mol^{-1}, h(C unsaturated) = –99909.44 kJ·mol^{-1}, h(H) = –1524.23 kJ·mol^{-1}, h(O) = –197138.05 kJ·mol^{-1}, h(N) = –143612.32 kJ·mol^{-1}, and h(F) = –26711.75 kJ·mol^{-1}.

As discussed above, the effective atomic enthalpy of sulfur will depend on the oxidation state. Additional problems may arise from sulfur-specific bonding configurations. For example, the S–S bond is a σ bond with a significantly decreased π antibonding compared to O-O due to the increased bond length; its description poses significant challenges even for modern high-level methods.[42] Direct evaluation of potentially needed high-level corrections would make the protocol more complex and may affect its efficiency. Instead, we propose a set of empirical corrections. Empirical group- and bond-additivity corrections were successfully used in the past, with applications ranging from semi-empirical methods[43] to MP4[44] and G3-theory composite methods.[45] The initial empirical model for the effective enthalpy of a sulfur atom was set to accommodate all anticipated patterns, with the intent to simplify its form based on statistical data analysis. Specifically, the effective enthalpy of a sulfur atom is defined as a base value, h(S), with the following corrections applied: S(IV), Δh(S(IV)); S(VI), Δh(S(VI)); S participating in a double bond, Δh(S=); aromatic S, Δh(S(arom)); S participating in the S–S bond, $\Delta h(\frac{1}{2}\text{SS})$; S forming an S–H bond, Δh(SH). For example, the effective enthalpy of a sulfur atom in H_2SO_4 is defined as $h = h(\text{S}) + \Delta h(\text{S(VI)}) + 2\Delta h(\text{S=})$.

In H_2S_2, $h = h(S) + \Delta h(\frac{1}{2}SS) + \Delta h(SH)$, for each S atom. This introduces seven potential empirical parameters to be established or eliminated.

Experimental data

To obtain a few kJ·mol^{-1} uncertainty in the enthalpy of formation, the uncertainty of the experimental combustion energy should be as low as a few hundredth percent. This requires state-of-the-art instruments, significant human expertise, and a multistep procedure for reduction of the experimental data to the standard conditions and $T = 298.15$ K. The current data reduction methodology was established in the mid-1950s,[24] and the data published prior to 1970 were revised by Cox and Pilcher.[46] In the subsequent analysis, we will use these revised values for the pre-1970 reports on sulfur compounds.

The values of auxiliary quantities used for data reduction have been significantly improved over the last six decades. However, in most studies, the 1956 recommendations[24] are still used. Recalculation of all experimental values with the best available recommendations[47] goes beyond the scope of this work, and it is not clear *a priori* whether the changes will be notable. Therefore, for all results published after 1970, we used the enthalpies of formation from the original analysis unless errors in data reduction were found.

Several dozens of sulfur compounds with sufficiently low repeatabilty-based expanded uncertainty (0.95 level of confidence) of the enthalpies of formation have been identified (Tables 4–9). Their chemical structures are shown in Figure 1. Only the compounds with a flexible backbone containing up to 5-6 heavy atoms are considered to avoid dealing with significant conformational ambiguity.

The list of laboratories having the largest contributions to the field includes NIPPR (Bartesville, Oklahoma), University of Lund (Sweden), Queen's University of Belfast (United Kingdom), University of Porto (Portugal), Institute of Physical Chemistry "Rocasolano" (Madrid, Spain), and Benemérita Universidad Autónoma de Puebla (Puebla, Mexico).

Enthalpies of vaporization or sublimation, which are required to convert the experimental condensed-phase enthalpies of formation to the gas-phase values, are often available from several works. For these properties, either weight-averaged or critically evaluated[48] experimental values were used.

After preliminary analysis of the experimental data, some values were excluded from the consideration because they ended up having large uncertainties. The remaining data were split into two parts, a training set and a testing set. The former had about 60 % of the considered organic and all inorganic compounds. The testing set primarily contained the results published after 2013 even if their repeatability-based uncertainty exceeded the threshold of 4 kJ·mol^{-1}.

Results and Discussion

In this section, small datasets are used to evaluate the effect of various factors on the computed results. This includes contributions beyond frozen-core CCSD(T), local approximation, and CBS extrapolation. This information gives one a better understanding of the accuracy potentially accessible with the protocol used. Then, a brief discussion of the available data for different groups of sulfur compounds is given. Finally, these results and conclusions are used to derive the effective enthalpies of sulfur, analyze performance of the protocol, and identify the problems and challenges with the experimental data.

Previously,[18] we analyzed energy contributions to atomization energies beyond frozen-core CCSD(T), ΔE^{hoc}, and contributions due to local CCSD(T) approximations, ΔE^{loc}, for CHON-containing molecules. These contributions were found to be well described by the atom-equivalent additivity approximation,

$$\Delta E^{\mathrm{X}}_{\mathrm{add}} = \sum_{\mathrm{types}} n_i e_i, \tag{5}$$

where, as in Eq. 1, n_i is atomic type count and e_i is an empirical constant obtained from

regression against ΔE^{X} data. The superscript "X" in the above notations is a placeholder used to distinguish the sources of contributions. In the following sections, we evaluate statistics of $(\Delta E^{\mathrm{X}}_{\mathrm{add}} - \Delta E^{\mathrm{X}})$ for the CHOS-containing compounds using a combination of data available from the literature and generated in this study. In addition, we analyze the effect of CBS extrapolation on the predictions.

Energy contributions beyond frozen-core CCSD(T)

The considered dataset is presented in Table 1. Most selected compounds have the W4.4, W4.2, or W4 results[49] available. For H_2SO_4, the core-valence, scalar relativistic, and spin-orbit contributions to the atomization energies are available[50] and included in the analysis. We also computed the latter contributions for two organic compounds, dimethyl sulfoxide and dimethyl sulfone. It was necessary to verify that the behavior of organic S(IV) and S(VI) compounds is similar to that of the inorganic counterparts and to clarify inconsistencies in the experimental data discussed below.

As follows from the results in Table 1, deviations from additivity for the post-CCSD(T) contributions do not exceed ± 1.0 kJ·mol^{-1}, which is acceptable for the expected uncertainty of ≈ 3 kJ·mol^{-1}. The deviations are significantly higher for other contributions reaching 2.1 and 1.7 kJ·mol^{-1} for the S(VI) compounds SO_3 and $(CH_3)_2SO_2$, respectively. However, such a large deviation is not observed for H_2SO_4.

For the compounds with all contributions known, the standard deviation for the ΔE^{hoc} deviations from additivity is greater than those of individual contributions considered above. This indicates that post-CCSD(T) and other higher-order corrections do not partially cancel one another. While the statistics is limited, the S(IV) compounds, SO_2 and SSO, have the largest negative deviations close to -1.4 kJ·mol^{-1}, the only S(VI) compound, SO_3, has the largest positive deviation of 2.8 kJ·mol^{-1}, and the S(II) compounds lie in-between.

Comparison of local and canonical CCSD(T) energies

The local and canonical CCSD(T)/aug-cc-pv(Q+d)Z energies for sulfur compounds are compared in Table 2. For flexible molecules exibiting multiple conformations, the computations were conducted for the lowest-energy conformer. In all cases except SO_3 and H_2SO_4, the local energies are more negative than their canonical counterparts. If one uses the C, H, and O atomic contributions obtained earlier,[18] the average difference between the additive and computed values is close to zero for the S(II) and S(IV) compounds. The S(VI) compounds have the deviations ranging from $-(1.4$ to $2.1)$ kJ·mol^{-1}. For SO_3, the deviation of -1.9 kJ·mol^{-1} is partially cancelled by a relatively large non-additivity of the ΔE^{hoc} term. Although comprehensive statistics is not available, one would expect that the corrections for different atomic types due to contributions beyond frozen-core CCSD(T) or the use of local approximation will be small for organosulfur compounds.

Finite basis set vs. complete basis set LCCSD(T) energies

CBS extrapolation of LCCSD(T) energies is potentially beneficial for the accuracy of the predicted $\Delta_{\mathrm{f}}H^{\circ}$values. In the protocol considered here, the QZ-quality basis set is used, and two two-point extrapolation schemes, TZ-QZ and QZ-5Z, are possible. The standard uncertainty of prediction with a TZ-quality basis set was 4.6 kJ·mol^{-1} as compared to 1.4 kJ·mol^{-1} with a QZ-based one.[17] The uncertainty will propagate to the extrapolated energy thus making the scheme unacceptable for the present accuracy requirements. This leaves the QZ-5Z extrapolation as the only choice. It significantly increases the computational time, which is critical for a protocol designed to be used on a scale of thousands molecules. Therefore, the use of extrapolation should be limited to the cases where it is truly needed.

Initially, the extrapolation was applied to the reference set of 42 CHON molecules used to parameterize this protocol.[18] The LCCSD(T)/CBS energies were then used to determine the effective enthalpies: h(C saturated or aromatic) = –99924.23 kJ·mol^{-1}, h(C unsaturated) = –99923.22 kJ·mol^{-1}, h(H) = –1525.10 kJ·mol^{-1}, h(O) = –197170.63 kJ·mol^{-1}, and h(N) =

-143634.18 kJ·mol^{-1}. The standard uncertainty of the prediction decreased insignificantly, from 1.25 kJ·mol^{-1} for the QZ version to 1.18 kJ·mol^{-1}. Therefore, the use of extrapolation with this protocol for CHON-compounds is not justified.

Inorganic species are used for analysis of sulfur compounds (Table 3) because their experimental enthalpies of formation are deemed most reliable. Some challenges with the experimental data for organic compounds containing S(IV) and S(VI) are discussed below. The effective enthalpies h(S) determined with the QZ basis set vary from (–7.5 to 8.9) kJ·mol^{-1} from the average value of –1044341.3 kJ·mol^{-1}. Two observations can be made based on these results. First, multiple corrections for different atomic types will be needed with this basis. Second, while Δh(SH) and Δh(S=) are expected to differ by about 2 kJ·mol^{-1}, Δh(S(IV)) and Δh(S(VI)) are expected to be about (10 to 15) kJ·mol^{-1} more positive.

The deviations from the average value $h(\mathrm{S}) = -1044370.3$ kJ·mol^{-1} for CBS energies are below ± 2 kJ·mol^{-1} and do not reveal any structure-related patterns. These deviations are comparable to the experimental uncertainties. Therefore, a single parameter for sulfur may be sufficient in this case to predict the enthalpy of formation for organosulfur compounds within the target accuracy. This also implies that, based on presented, albeit rather limited, statistics, the basis set size appears to be a dominant factor for describing sulfur-containing compounds with chemical accuracy within an atom-equivalent additivity scheme. The same applies to calculation of reaction enthalpies, especially those involving compounds with different oxidation states of sulfur: accurate results would require the basis sets well above the quadruple-zeta quality, which would rule out many popular composite budget methods.

Thiols and sulfides

Most results for thiols and a significant portion of data for sulfides originate from the Bartesville laboratory. Some measurements were conducted at Lund, Belfast, and Madrid. We estimated the lower uncertainty limit of our predictions using values from Tables 4 and 5. Two preliminary parameters, h(S) = –1044348.6 kJ·mol^{-1} and Δh(SH) = –1.2 kJ·mol^{-1},

were found by the least-squares fitting of experimental data with Eq. 1 and LCCSD(T)/aug-cc-pV(Q+d)Z energies. The standard uncertainty of the fit was 1.3 kJ·mol^{-1}. Therefore, in the best-case scenario, the enthalpies of formation for the sulfur-containing substances can be predicted within ∼2.6 kJ·mol^{-1} with a 0.95 probability. This estimate is comparable to the expanded uncertainty of about 3 kJ·mol^{-1} estimated for the enthalpies of formation of medium-sized CHON-compounds predicted with this method.[18] This also provides the scale for accessing the quality of CHONS experimental data. If the experimental $\Delta_f H^\circ$ for a compound significantly deviates from the predicted value, uncertainty of the experimental value should be increased and the value itself should not be used for parameterization of the method.

The results from Lund are in excellent agreement with those from Bartesville. The agreement with the results from Belfast is somewhat worse: for benzylthiol, methyl phenyl sulfide, and diphenyl sulfide, the differences are (5 to 8) kJ·mol^{-1}. Considering problems with the results for oxygenated compounds from this laboratory described below, the results from Bartesville were favored in these cases.

The gas-phase enthalpies of formation of 1,3-[51] and 1,4-dithiacyclohexanes[52] and 1,3,5-trithiacyclohexane[53] were reported by the Madrid team. The sublimation enthalpies of the dithiacyclohexanes derived from the temperature-dependent vapor pressures significantly deviate from those obtained from similar measurements by De Wit et al.[54] Comparison with the *ab initio* results suggests that the latter is likely preferable. 1,3,5-trithiacyclohexane is prone to polymerization at the conditions of sublimation experiments,[54] and partial polymerization in the combustion experiments cannot be fully ruled out. Consequently, the experimental $\Delta_f H^\circ$value for this compound was excluded.

Disulfides and aromatic sulfur substances

Short-chain dialkyl disulfides were studied in Bartesville.[55,56] For isomeric dibutyl disulfides, the data from Belfast are available.[57] The measurements for di-*tert*-butyl derivative

were conducted in both laboratories. In this work, the dimethyl, diethyl, and di-*tert*-butyl derivatives are considered. In addition, the enthalpy of formation of diphenyl disulfide was recentely revised by Ramos et al.[58] This improved value is used here in the training set and two diaminodiphenyl derivatives from the same work were included in the test set.

Sulfur is a part of an aromatic ring in thiophenes, thiazoles, and isothiazoles. The $\Delta_f H^\circ$ data are available for the former two groups. To maximize the diversity of the aromatic groups, multiple thiophene and thiazole derivatives were included in the training set (Table 6). These results were mostly obtained in the Bartesville and Porto laboratories.

Substances with sulfur double bonds, S(IV), and S(VI)

Organic compounds containing S(IV) and S(VI) typically have S=O bonds, while a C=S bond is normally seen in the S(II) compounds. The compounds with a C=S bond have been actively investigated over the past five years.[59–63] The S(IV) and S(VI) compounds for which the $\Delta_f H^\circ$values are available include sulfoxides, sulfones, sulfites, sulfates, and sulfonamides. Dozens of compounds of this group have been studied. Unfortunately, the number of reliable $\Delta_f H^\circ$values for the gas phase is surprisingly low. Those for dimethyl sulfoxide[64,65] and thiacyclopentane 1,1-dioxide (sulfolane)[66] included in the training set are the only reliable values that we are aware of. The enthalpy of vaporization reported for the latter was revised using the ideal-gas enthalpies computed in this work. Inconsistencies between the computed and experimental data for this group are discussed below.

Inorganic species

The enthalpies of formation for gaseous H_2S and SO_2 recommended by CODATA[67] were used in this work. $\Delta_f H^\circ_m$ of SSO, SO_3, CS_2, COS, H_2SO_4 were taken from Ref. 68. The JANAF[69,70] values for SO_2, H_2S, SSO, SO_3, CS_2, and H_2SO_4 are consistent with the recommendations above. However, the JANAF value for COS is 3.3 kJ·mol^{-1} less negative than the more recent one. $\Delta_f H^\circ_m(S_8(g))$ is equal to the enthalpy of sublimation of rhombic

sulfur. This value was derived using the temperature-dependent vapor pressures available in multiple works. The sublimation enthalpy of S_8 and its uncertainty was evaluated in this work using the original data[71,72] and $\Delta_{\mathrm{subl}}C_P = -26$ J·K^{-1}·mol^{-1}.[73]

Fehèr *et al.* published a series of papers on thermodynamic properties of hydrogen polysulfides. Out of these compounds, H_2S_2 is considered here. The enthalpy of its decomposition[74] H_2S_2(l) = H_2S(g) + 1/8 S_8(rh) at atmospheric pressure was combined with the calorimetrically determined vaporization enthalpy[75] and the CODATA value of $\Delta_{\mathrm{f}}H^{\circ}_{\mathrm{m}}(H_2S(g))$ to obtain $\Delta_{\mathrm{f}}H^{\circ}_{\mathrm{m}}(H_2S_2(g))$. Some properties were reported at $T = 293$ K and adjusted to $T = 298$ K using the gas-phase heat capacities of S(rh) and H_2S(g) recommended by CODATA and $C_p(H_2S_2)$ calculated in this work.

Final regression and comparison with experimental data

During the parameter fitting procedure, equations for each compound were set on per sulfur atom basis. This was necessary to avoid the bias toward compounds with the number of sulfur atoms greater than one (*e.g.* S_8). Initially, seven parameters described above were considered. Following the analysis, the Δh(SH) value was found to be statistically insignificant. The difference between Δh(S(arom)) and Δh(S=) was very small, below 0.2 kJ·mol^{-1}. The difference with $\Delta h(\frac{1}{2}\mathrm{SS})$ was close to 0.3 kJ·mol^{-1}, and also not statistically significant. Therefore, these three parameters were combined into one. Finally, the definitive estimation of Δh(S(IV)) and Δh(S(VI)) was challenging as the amount of reliable data for the S(IV) and S(VI) compounds is extremely limited. Form the initial analysis, it was found that Δh(S(VI)) is approximately twice as large as Δh(S(IV)) and, instead of having two independent parameters, the ratio $\Delta h(\mathrm{S(IV)}) = \frac{1}{2}\Delta h(\mathrm{S(VI)})$ was imposed.

The final least-squares fit of the experimental data with these three parameters resulted in the following values:

h(S) = -1044348.68 kJ·mol^{-1}

$\Delta h(\mathrm{S{=}}) = \Delta h(\frac{1}{2}\mathrm{SS}) = \Delta h(\mathrm{S(arom)}) = 1.76$ kJ·mol^{-1}

$\Delta h(\mathrm{S(IV)}) = \frac{1}{2}\Delta h(\mathrm{S(VI)}) = 5.03$ kJ·mol^{-1}

The computed values are compared with their experimental counterparts in Figures 2, 3, and 4. Generally, the computed values are in a very good agreement with the experiments, with the standard deviation for the training set of 1.8 kJ·mol^{-1}. For the testing set, the standard deviation is 4.8 kJ·mol^{-1}, mainly because of five outliers in recent publications (Table 9). It comes close to that of the training set, 2.3 kJ·mol^{-1}, if they are removed.

A single parameter, $h(\mathrm{S}) = -(1044371.95 \pm 0.30)$ kJ·mol^{-1}, was found to be statistically significant for the CBS version. The computed and experimental values are compared in Figures 5 and 6. The standard deviation of 2.2 kJ·mol^{-1} for the training set becomes 4.3 and 2.5 kJ·mol^{-1} for the testing set with the outliers and without them, respectively. Typically, the deviations between two versions is within 1.5 kJ per mole of sulfur atoms. Notable differences between the predictions are observed for disulfur monoxide (3.4 kJ·mol^{-1}) and sulfur trioxide (3.0 kJ·mol^{-1}). The reason of this behavior is unclear.

The expanded uncertainty can be estimated as follows:

$$U(\Delta_{\mathrm{f}} H^{\circ}_{\mathrm{m}}) = \sqrt{U^2(\mathrm{CHON}) + (U(h(\mathrm{S}))n(\mathrm{S}))^2} \tag{6}$$

The first term in the right-hand side of Eq. 6 is a contribution associated with C, H, O, and N atoms and evaluated as described earlier.[18] This contribution includes uncertainty of the model as well as uncertainties of the effective enthalpies of atoms. For the considered compounds, $U(\mathrm{CHON})$ is close to (2.5 to 3.0) kJ·mol^{-1}. $U(h(\mathrm{S})) = 0.6$ kJ·mol^{-1} for the CBS version of the protocol. While a rigorous evaluation is not possible, we also expect the uncertainty for the QZ version to be close to this value.

The results obtained with the QZ version of the protocol will be used in further analysis. The use of the CBS results leads to similar conclusions.

A relatively large deviation of 7.4 kJ·mol^{-1} is observed for 4,4'-disulfanediyldianiline while the deviation for the 2,2'- isomer is only 2.0 kJ·mol^{-1}. The computed enthalpies of formation

for two 1,3-dihydro-2H-benzimidazole-2-thione derivatives deviate from the experimental values reported by Perdomo *et al.*[62] by about 6 kJ·mol^{-1}. The $\Delta_f H^\circ$ value for the third compound from that work, 1-methyl-1,3-dihydro-2H-imidazole-2-thione, is consistent with the computations. The computed $\Delta_f H^\circ$for 1,3-dihydro-2H-benzimidazole-2-thione itself is in good agreement with the experimental[61] value reported by the Porto lab. Also, it was supported by the G3-theory computations in the original work.

Silva *et al.*[76] reported the enthalpies of formation of three benzothiazole derivatives. A good agreement between the computed and experimental values is observed for benzothiazole and 2,5-dimethylbenzothiazole (Table 6). However, the unexpected difference of 14 kJ·mol^{-1} is seen for the 2-methyl derivative. Thus, we believe the computed value should be preferred for the latter. The deviation for 5-fluoro-2-methylbenzothiazole is about 9 kJ·mol^{-1}. This compound is unusual for the combustion measurements because it has both fluorine and sulfur atoms. As such, some reference values required to adjust the experimental results to the standard state are not available in the literature. Thus, the comparison experiments had to be used to derive the $\Delta_f H^\circ$value, likely causing an increase in uncertainty. Considering all these factors, the 9 kJ·mol^{-1} difference appears satisfactory.

The reason for a -6.0 kJ·mol^{-1} difference for phenoxathiin is unclear. Although the sublimation enthalpy of this compound have been measured in several works, its combustion energy has been reported only once.[77] Additional measurements would be very helpful.

Based on their own G3-theory calculations, the authors of the original publication on 1,3-dihydroimidazole-2-thione[63] have also concluded that their $\Delta_f H^\circ_m(g)$ value is about 30 kJ·mol^{-1} higher than the *ab initio* result. The inconsistency was explained by suggesting formation of the thiol tautomer whose $\Delta_f H^\circ$was in excellent agreement with the calculations. However, the combustion experiments were conducted with the crystalline sample, and the crystal phase was confirmed to contain the thione form.[63] Formation of the tautomer with the Gibbs energy of about 30 kJ·mol^{-1} in the sublimation experiments does not appear plausible, and, again, new experimental data on the gas-phase composition of this compound

would be beneficial to address the existing inconsistency.

Further, the problems with the enthalpies of formation of the S(IV) and S(VI) compounds are discussed. For dimethyl sulfone (methylsulfonyl methane), two consistent values for the solid-phase $\Delta_f H^\circ$have been published.[64,78] The enthalpy of sublimation needed to convert this solid-phase value to the gas-phase $\Delta_f H^\circ$was derived in this work as follows. Vapor pressure over the liquid sulfone was measured using a Bourdon gauge as a null manometer in the temperature range of (385 to 523) K and reported in the form of the Antoine equation.[79] If one neglects non-ideality of the gas phase, the enthalpy of vaporization is estimated from vapor pressure slope as $\Delta_{vap} H_m(454\ \mathrm{K}) = (54.2 \pm 1.3)\ \mathrm{kJ{\cdot}mol^{-1}}$. The enthalpy difference $H_m(\mathrm{l}, 454\ \mathrm{K}) - H_m(\mathrm{cr}, 298\ \mathrm{K}) = 43.2\ \mathrm{kJ{\cdot}mol^{-1}}$ can be determined using the linearly extrapolated calorimetric data of Clever and Westrum.[80] The gas-phase enthalpy change, $H_m(\mathrm{g}, 454\ \mathrm{K}) - H_m(\mathrm{g}, 298\ \mathrm{K}) = 18.2\ \mathrm{kJ{\cdot}mol^{-1}}$ was calculated using the present theoretical model described above. The final enthalpy of sublimation obtained in this manner is $\Delta_{subl} H_m(298\mathrm{K}) = (79.2 \pm 1.4)\ \mathrm{kJ{\cdot}mol^{-1}}$. The resulting estimated uncertainty is fairly low; yet, a large difference between the computed and experimental $\Delta_f H_m^\circ(\mathrm{g})$ value exists. It is most likely caused by $\Delta_{subl} H_m$ value and the issue can only be resolved by performing new measurements, corroborating or rejecting the available limited data.[79] The temperature-dependent vapor pressures of this compound were recently estimated using thermogravimetric analysis and reported as coefficients of the Antoine equation.[81] An unphysical value of +958 K reported for the C coefficient indicates that these results are in error.

The enthalpies of formation of other aliphatic and aromatic sulfones were determined in the Belfast lab. Some original data for sulfones have never been published and are only available in the review of Cox and Pilcher.[46] Di-n-alkyl sulfones are considered here as an example (Figure 7). The experimental increment of the gas-phase $\Delta_f H^\circ$ per CH_2 group varies from $-(8$ to $36)\ \mathrm{kJ{\cdot}mol^{-1}}$ between different homologues. According to the computations in this work, it is close to $-24\ \mathrm{kJ{\cdot}mol^{-1}}$ for the short-chain compounds ($n(\mathrm{C}) < 5$). For the longer alkyl chains, the increment similar to that of n-alkanes (about 21 $\mathrm{kJ{\cdot}mol^{-1}}$) is

expected. No notable systematic shift between the computed and experimental values is observed (Figure 7). However, significant data scatter indicates that the expanded uncertainty of the experimental data should be close to 10 kJ·mol^{-1}.

The only work on sulfites and sulfates was published by Mackle and Steele.[82] The experimental increment per CH_2 group varies from −(28 to 41) kJ·mol^{-1} for the short-chain homologues compared to −34 and −35 kJ·mol^{-1} computed for the sulfites and sulfates, respectively. Because of significant data scatter, it cannot be concluded whether the systematic deviations between the computed and experimental values are due to incorrect h(S) or large experimental uncertainties. Consequently, the data on sulfones, sulfites, and sulfates were excluded from further consideration. This leaves sulfuric acid as the only compound with both S=O and S-O bonds that has a reliable value of $\Delta_f H^\circ$. Generation of new experimental data for organic sulfites and sulfates is critical to closing this neglected gap in thermochemistry of sulfur and would contribute greatly to the development and validation of theoretical methods.

The energy of combustion of another candidate, benzenesulfonamide, has been reported in two works.[83,84] With the use the enthalpy of sublimation from Ref. 83, the values of the resulting gas-phase enthalpies of formation from two sources differ by 23 kJ·mol^{-1}. Comparison with the prediction of the current model suggests that the result of Matos et al.[83] is more favorable (−5 kJ·mol^{-1} deviation), while the value of Flores et al.[84] shows the deviation of 18 kJ·mol^{-1}.

Thiacyclohexane 1,1-dioxide[85] has a −9.8 kJ·mol^{-1} deviation from the experimental value. The computed enthalpies of formation for similar compounds have a −9 kJ·mol^{-1} average deviation from the experimental values[86–89] originating from the same laboratory. The origins of this behavior are unclear and also need to be resolved by conducting new measurements.

From the major data contributors discussed above, only the laboratories in Porto and Puebla are still active. The computed $\Delta_f H^\circ$ values are compared with experimental data

published by these two groups after 2013 (Figure 4). For three values from the Porto lab and one value (benzenesulfonamide) from Puebla, the deviations exceed +9 kJ·mol^{-1} (all are discussed above). The other experimental results are consistent with the expected expanded uncertainty of the predicted values, 3 kJ·mol^{-1}. The data from Porto are scattered around zero with the average deviation of 0.6 kJ·mol^{-1}. The results from the Puebla lab are systematically more negative than the predictions with the average deviation of 4.1 kJ·mol^{-1}.

Summary

The extension of our previously developed LCCSD(T)-based protocol[18] for prediction of the gas-phase $\Delta_{\mathrm{f}}H^{\circ}$ for closed-shell compounds to sulfur-containing compounds is presented. It shares the computational efficiency of the original formulation, thus allowing rapid evaluation and large-scale processing applications. The accuracy and generalization of the method is hindered by (somewhat unexpectedly) limited amount of reliable data for the diverse classes of sulfur-containing organic compounds. Numerous, from obvious to suspected, experimental issues have been identified. Furthermore, surprising gaps in data coverage for compound classes of both practical and scientific interest (*e.g.*, sulfites and sulfates) were found. This causes problems in model parametrization as well as in its proper validation and accuracy assessment.

Formal comparison with a large set of available data critically-evaluated in this work yields the standard deviation of about 2 kJ·mol^{-1}, suggesting a 95% confidence uncertainty of about 4 kJ·mol^{-1}. This value, however, represents an upper estimate. The actual uncertainty, considering the scatter in the experimental data, is likely to be closer to 3 kJ·mol^{-1}, as evidenced by the analysis of the data subsets exhibiting lower levels of experimental uncertainties.

Table 1: Sum of contributions beyond frozen-core CCSD(T) ($\Delta E^{\mathbf{hoc}}$), post-CCSD(T) contributions ($\Delta E^{\mathbf{post}}$), contributions other than post-CCSD(T) to atomization energy ($\Delta E^{\mathbf{hoc}} - \Delta E^{\mathbf{post}}$), and their deviations from the atom-equivalent additivity, kJ·mol^{-1}

compound	protocol	ΔE^{hoc}	dev.[a]	ΔE^{post}	dev.[a]	$\Delta E^{\mathrm{hoc}} - \Delta E^{\mathrm{post}}$	dev.[a]
hydrogen	W4.4	0.08	-0.04	0.00	-0.11	0.08	0.06
water	W4.4	-0.12	-0.71	-0.08	0.19	-0.04	-0.90
methane	W4.4	4.48	-0.13	0.04	-0.17	4.44	0.04
ethyne	W4.4	9.50	-0.93	0.42	-0.35	9.08	-0.57
carbon monoxide	W4.4	2.64	0.75	0.38	-0.08	2.26	0.83
hydrogen sulfide	W4.4	-2.18	0.97	0.29	0.76	-2.47	0.21
ethene	W4.2	8.58	0.03	0.08	-0.13	8.49	0.16
methanal	W4.2	3.31	0.12	0.33	-0.14	2.97	0.27
carbon dioxide	W4.2	3.77	-1.26	0.25	0.26	3.51	-1.51
hydrogen peroxide	W4.2	-0.38	-1.33	1.00	-0.69	-1.38	-0.65
ethane	W4	7.95	0.70	-0.46	0.31	8.41	0.39
sulfur dioxide	W4	-1.80	-1.20	1.76	-0.17	-3.56	-1.03
sulfur trioxide	W4	-6.65	2.77	1.17	0.63	-7.82	2.15
carbon oxide sulfide	W4	1.30	0.84	1.17	0.29	0.13	0.55
carbon disulfide	W4	1.72	0.05	2.22	0.19	-0.50	-0.14
disulfur monoxide	W4	-1.63	-1.74	3.47	-0.94	-5.10	-0.80
sulfuric acid	[b]					-6.78	0.16
dimethyl sulfoxide	this work					5.01	0.29
dimethyl sulfone	this work					2.52	1.70
Standard deviation			1.28		0.49		0.98

[a] Additive value minus the computed value; [b] Ref. 50

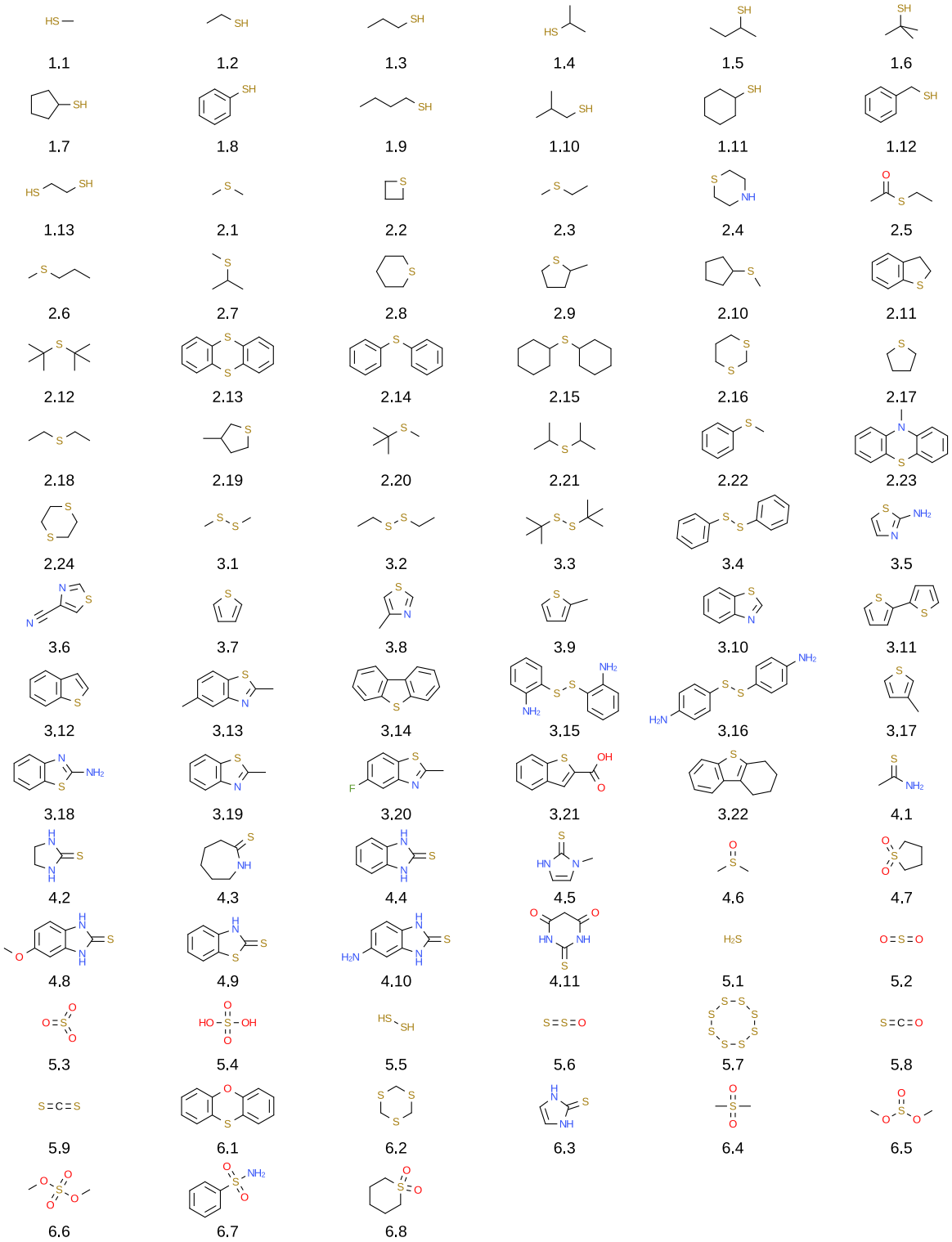

Figure 1: Chemical structures and identifiers of compounds considered in this work. The compound identifiers correspond to those in Tables 4–9.

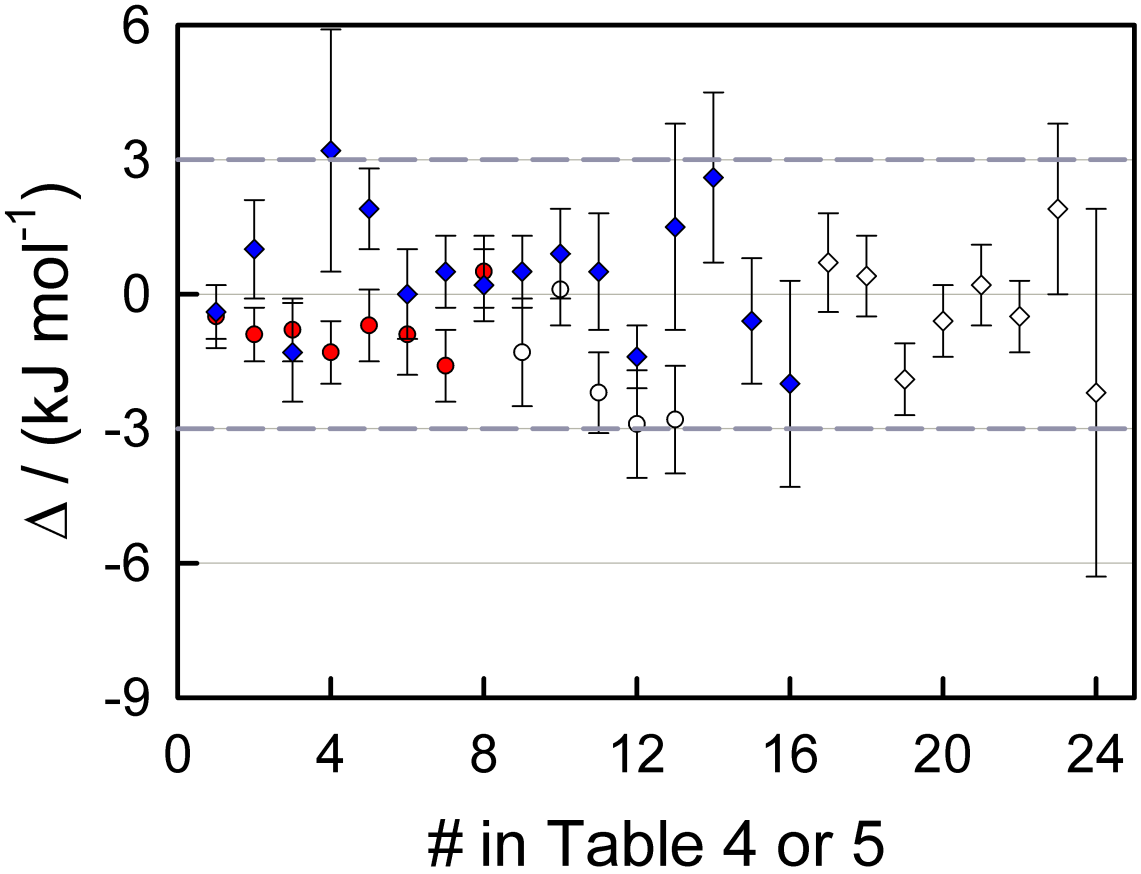

Figure 2: Comparison of the computed (QZ version) and experimental enthalpies of formation for thiols (circles) and sulfides (diamonds). Filled and empty symbols are used for the training and testing set, respectively.

Table 2: Deviations of local CCSD(T) energies from canonical values

compound	E(canonical) / Hartree	ΔE^{loc} / (kJ·mol^{-1})^a	dev. / (kJ·mol^{-1})^b
hydrogen sulfide	-398.958965	-0.3	0.2
sulfur dioxide	-548.062961	-0.5	-0.1
sulfur trioxide	-623.191638	0.9	-1.9
carbon oxide sulfide	-510.976509	-1.0	0.2
carbon disulfide	-833.561382	-0.4	0.0
disulfur monoxide	-870.653730	-0.9	0.6
sulfuric acid	-699.594130	0.7	-2.1
dimethyl sulfoxide	-552.588746	-1.2	-0.5
dimethyl sulfone	-627.764576	-0.6	-1.4
Standard deviation		0.7	1.5

^{a} $\Delta E^{\mathrm{loc}} = E(\mathrm{local}) - E(\mathrm{canonical})$. ^{b} Additive value minus the computed value. The additive values were found as[18] $\Delta E^{\mathrm{loc}}_{\mathrm{add}}$ kJ·mol^{-1}= $-0.46n_{\mathrm{C}} - 0.07n_{\mathrm{H}} - 0.32n_{\mathrm{O}}$

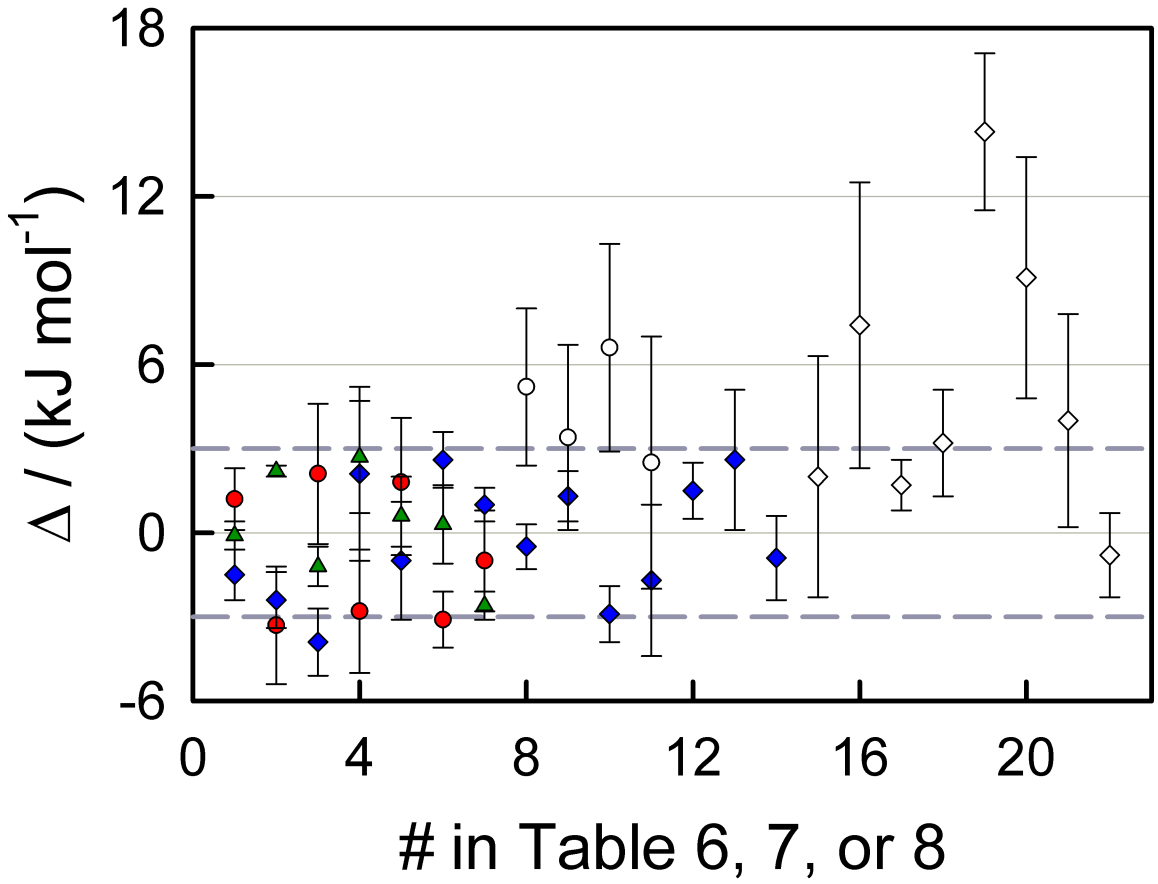

Figure 3: Comparison of the computed (QZ version) and experimental enthalpies of formation for compounds with the sulfur double bond, S(IV), and S(VI) (circles); disulfides and aromatic compounds (diamonds); and inorganic compounds (triangles). Filled and empty symbols are used for the training and testing set, respectively.

Table 3: Effect of basis set extrapolation on the effective enthalpy of sulfur

compound	Exp. $\Delta_f H^\circ_m$(g) / (kJ·mol^{-1})	Δ(QZ) / (kJ·mol^{-1})^a	Δ(CBS) / (kJ·mol^{-1})^b
hydrogen sulfide	$-(20.6 \pm 0.5)$	-7.5	-1.5
sulfur dioxide	$-(296.8 \pm 0.2)$	3.3	1.9
sulfur trioxide	$-(395.9 \pm 0.7)$	6.7	0.1
carbon oxide sulfide	$-(141.7 \pm 2.0)$	-5.2	-0.4
carbon disulfide	116.7 ± 1.0	-5.7	-1.2
disulfur monoxide	$-(56.0 \pm 1.4)$	-0.4	1.7
sulfuric acid	$-(732.7 \pm 2.0)$	8.9	-0.5

^{a} deviation from the average value of h(S) = -1044341.3 kJ·mol^{-1}; ^{b} deviation from the average value of h(S) = -1044370.3 kJ·mol^{-1}

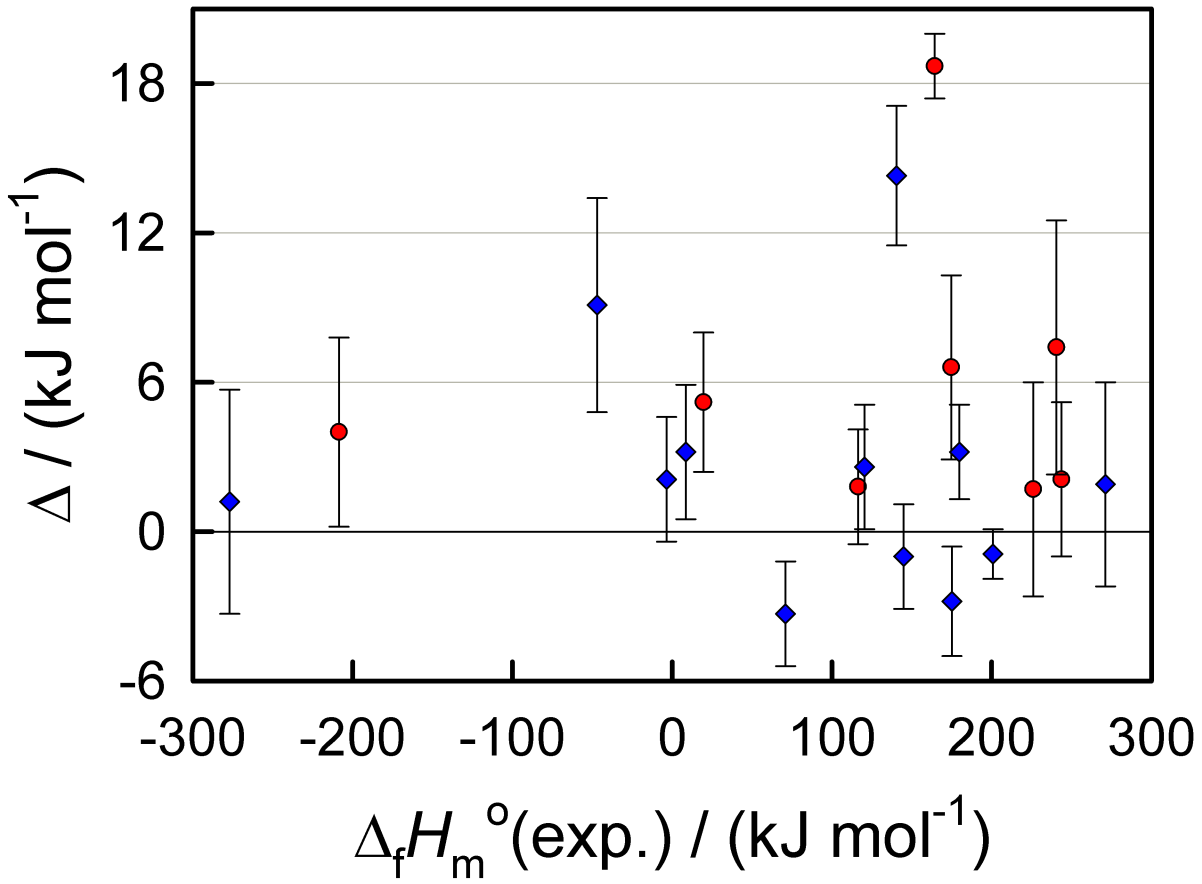

Figure 4: Comparison of the computed (QZ version) and experimental enthalpies of formation of compounds, for which the combustion energies were published after 2013: diamonds, determined in the Porto laboratory;[59–61,63,76,90–94] circles, determined in the Puebla laboratory.[58,62,95,96] The value for 1,3-dihydroimidazole-2-thione has a deviation of -32 kJ·mol^{-1}and is not shown

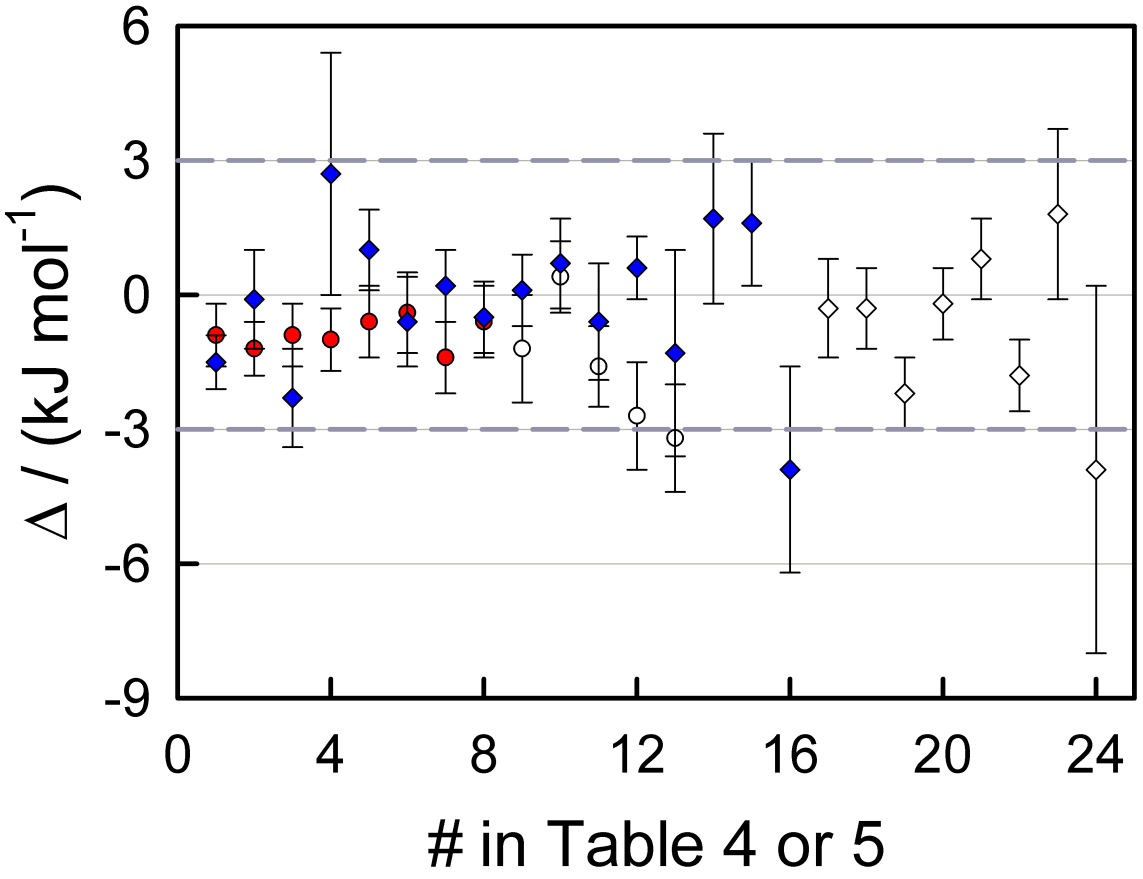

Figure 5: Comparison of the computed (CBS version) and experimental enthalpies of formation for thiols (circles) and sulfides (diamonds). Filled and empty symbols are used for the training and testing set, respectively.

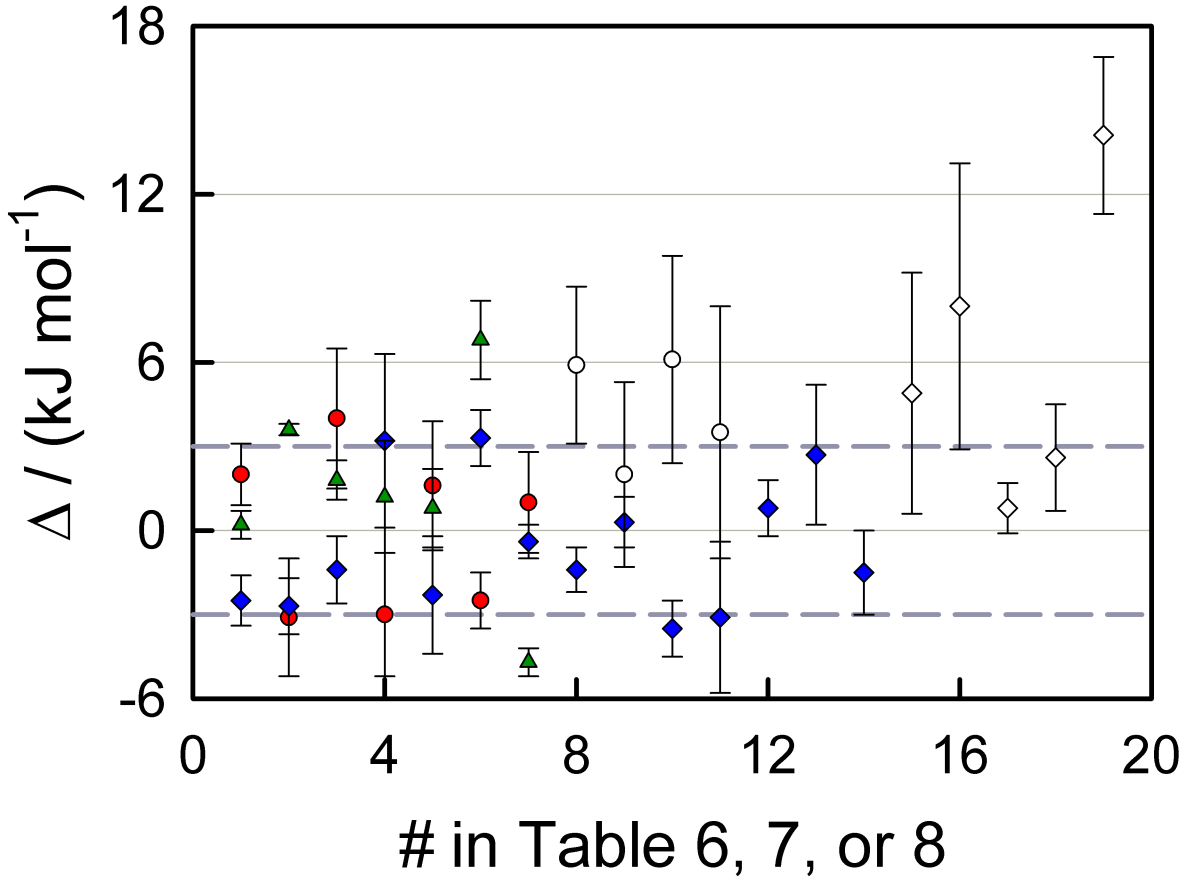

Figure 6: Comparison of the computed (CBS version) and experimental enthalpies of formation for compounds with the sulfur double bond, S(IV), and S(VI) (circles); disulfides and aromatic compounds (diamonds); and inorganic compounds (triangles). Filled and empty symbols are used for the training and testing set, respectively.

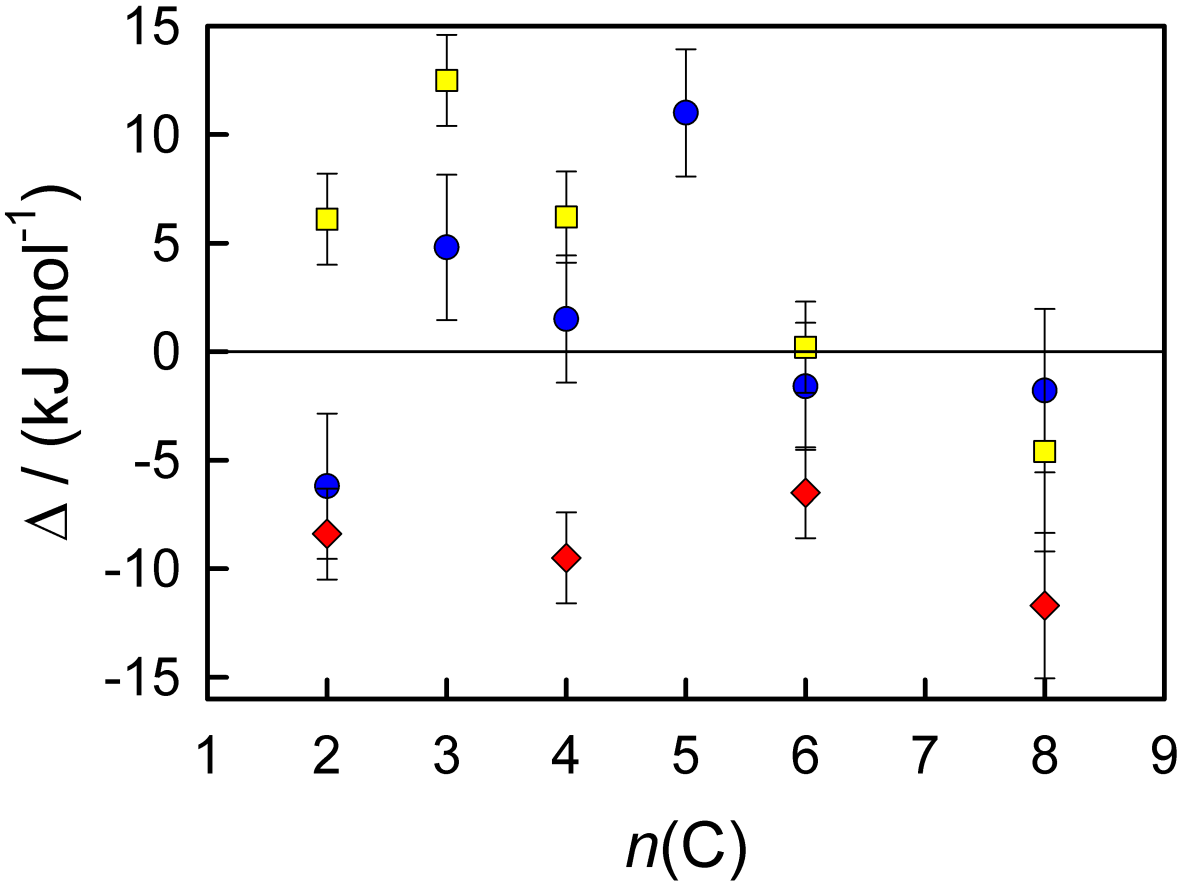

Figure 7: Deviation of the estimated enthalpies of formation of normal dialkyl sulfones (blue circles), sulfites (yellow squares), and sulfates (red diamonds) from their experimental counterparts as a function of carbon atom number. The experimental values obtained in the Belfast lab are taken from the compilation of Cox and Pilcher.[46] The original data were partially published in Refs. 78, 79, 82, and 97. The repeatability-based expanded uncertainties stated by the authors are shown. The enthalpies of formation at $n < 5$ and for n-propyl sulfate were computed using the QZ version of the protocol described in this work. The values at other n were estimated using a -21 kJ·mol^{-1} increment per CH_2 group.

Table 4: Thermochemical properties of thiols at $T = 298$ K

Chemical Name	CASRN	Phase at T	Exp. $\Delta_f H^\circ_m(g)$ / kJ·mol^{-1}	References[a]	Δ(QZ)[b] / kJ·mol^{-1}	Δ(CBS)[b] / kJ·mol^{-1}
			Training set			
methanethiol (**1.1**)	74-93-1	l[c]	$-(22.3 \pm 0.7)$	98; 48	-0.5	-0.9
ethanethiol (**1.2**)	75-08-1	l	$-(46.0 \pm 0.6)$	99; 48	-0.9	-1.2
1-propanethiol (**1.3**)	107-03-9	l	$-(67.7 \pm 0.7)$	100; 48	-0.8	-0.9
2-propanethiol (**1.4**)	75-33-2	l	$-(75.9 \pm 0.7)$	100; 101	-1.3	-1.0
2-butanethiol (**1.5**)	513-53-1	l	$-(96.6 \pm 0.8)$	102; 103	-0.7	-0.6
2-methyl-2-propanethiol (**1.6**)	75-66-1	l	$-(109.3 \pm 0.9)$	102; 104	-0.9	-0.4
cyclopentanethiol (**1.7**)	1679-07-8	l	$-(47.7 \pm 0.8)$	105	-1.6	-1.4
benzenethiol (**1.8**)	108-98-5	l	112.7 ± 0.8	106; 106: 107	0.5	-0.6
			Testing set			
1-butanethiol (**1.9**)	109-79-5	l	$-(87.8 \pm 1.2)$	102; 108,109	-1.3	-1.2
2-methyl-1-propanethiol (**1.10**)	513-44-0	l	$-(96.9 \pm 0.8)$	102; 110	0.1	0.4
cyclohexanethiol (**1.11**)	1569-69-3	l	$-(95.7 \pm 0.9)$	56; 111,112	-2.2	-1.6
phenylmethanethiol (**1.12**)	100-53-8	l	93.5 ± 1.2	56: 113; 114	-2.9	-2.7
1,2-ethanedithiol (**1.13**)	540-63-6	l	$-(9.0 \pm 1.2)$	115	-2.8	-3.2

[a] Sources of combustion or reaction energies used to derive the condensed-phase $\Delta_f H^\circ_m$ and sources of enthalpies of sublimation or vaporization are separated by semicolon. Unused sources (if any) are listed after colon for each field; [b] $\Delta = \Delta_f H^\circ_m$(calc) - $\Delta_f H^\circ_m$(exp); [c] at bomb conditions

Table 5: Thermochemical properties of sulfides at $T = 298$ K

Chemical Name	CASRN	Phase at T	Exp. $\Delta_f H^\circ_m(g)$ / kJ·mol^{-1}	References[a]	Δ(QZ)[b] / kJ·mol^{-1}	Δ(CBS)[b] / kJ·mol^{-1}
			Training set			
2-thiapropane (**2.1**)	75-18-3	l	$-(37.4 \pm 0.6)$	99,116; 48	-0.4	-1.5
thiacyclobutane (**2.2**)	287-27-4	l	61.0 ± 1.1	117,118; 119	1.0	-0.1
2-thiabutane (**2.3**)	624-89-5	l	$-(59.3 \pm 1.1)$	100; 120	-1.3	-2.3
thiomorpholine (**2.4**)	123-90-0	l	8.6 ± 2.7	90	3.2	2.7
S-ethyl ethanethioate (**2.5**)	625-60-5	l	$-(227.8 \pm 0.9)$	121; 122	1.9	1.0
2-thiapentane (**2.6**)	3877-15-4	l	$-(81.9 \pm 1.0)$	102; 108	0.0	-0.6
3-methyl-2-thiabutane (**2.7**)	1551-21-9	l	$-(90.2 \pm 0.8)$	102; 123	0.5	0.2
thiacyclohexane (**2.8**)	1613-51-0	l	$-(63.3 \pm 0.8)$	118,124; 124	0.2	-0.5
2-methylthiacyclopentane (**2.9**)	1795-09-1	l	$-(63.9 \pm 0.8)$	56; 56,111	0.5	0.1
cyclopentyl-1-thiaethane (**2.10**)	7133-36-0	l	$-(64.3 \pm 1.0)$	56; 56,111	0.9	0.7
2,3-dihydrobenzo[b]thiophene (**2.11**)	4565-32-6	cr	108.5 ± 1.3	125	0.5	-0.6
2,2,4,4-tetramethyl-3-thiapentane (**2.12**)	107-47-1	l	$-(188.6 \pm 0.7)$	56,126; 127: 128	-1.4	0.6
thianthrene (**2.13**)	92-85-3	cr	288.5 ± 2.3	129; 77,130: 131–133	1.5	-1.3
diphenyl sulfide (**2.14**)	139-66-2	l	229.3 ± 1.9	134: 135; 134,136	2.6	1.7
dicyclohexyl sulfide (**2.15**)	7133-46-2	l	$-(182.8 \pm 1.4)$	137; 138	-0.6	1.6
1,3-dithiacyclohexane (**2.16**)	505-23-7	cr	6.2 ± 2.3	51; 54: 51	-2.0	-3.9
			Testing set			
thiacyclopentane (**2.17**)	110-01-0	l	$-(33.6 \pm 1.1)$	117,139; 139,140	0.7	-0.3
3-thiapentane (**2.18**)	352-93-2	l	$-(83.4 \pm 0.9)$	102,116; 48	0.4	-0.3
3-methylthiacyclopentane (**2.19**)	4740-00-5	l	$-(60.2 \pm 0.8)$	56; 56,111	-1.9	-2.2
3,3-dimethyl-2-thiabutane (**2.20**)	6163-64-0	l	$-(121.0 \pm 0.8)$	141	-0.6	-0.2
2,4-dimethyl-3-thiapentane (**2.21**)	625-80-9	l	$-(141.6 \pm 0.9)$	56,126; 48	0.2	0.8
1-phenyl-1-thiaethane (**2.22**)	100-68-5	l	97.6 ± 0.8	56: 128	-0.5	-1.8
N-methylphenothiazine (**2.23**)	1207-72-3	cr	271.3 ± 4.1	92	1.9	1.8
1,4-dithiacyclohexane (**2.24**)	505-29-3	cr	1.8 ± 2.4	52; 54: 52	-2.2	-3.9

[a] Sources of combustion or reaction energies used to derive the condensed-phase $\Delta_f H^\circ_m$ and sources of enthalpies of sublimation or vaporization are separated by semicolon. Unused sources (if any) are listed after colon for each field; [b] $\Delta = \Delta_f H^\circ_m$(calc) - $\Delta_f H^\circ_m$(exp), kJ·mol^{-1}

Table 6: Thermochemical properties of disulfides and compounds with an aromatic sulfur atom at $T = 298$ K

Chemical Name	CASRN	Phase at T	Exp. $\Delta_f H^\circ_m(g)$ / kJ·mol^{-1}	References[a]	Δ(QZ)[b] / kJ·mol^{-1}	Δ(CBS)[b] / kJ·mol^{-1}
			Training set			
2,3-dithiabutane (**3.1**)	624-92-0	l	$-(23.8 \pm 0.9)$	55,116; 48	-1.5	-2.5
3,4-dithiahexane (**3.2**)	110-81-6	l	$-(74.2 \pm 1.0)$	55,116; 116,142,143	-2.4	-2.7
2,2,5,5-tetramethyl-3,4-dithiahexane (**3.3**)	110-06-5	l	$-(199.4 \pm 1.2)$	56,144; 143	-3.9	-1.4
diphenyl disulfide (**3.4**)	882-33-7	cr	243.7 ± 3.1	58: 135,145; 58	2.1	3.2
2-aminothiazole (**3.5**)	96-50-4	cr	144.9 ± 2.1	91	-1.0	-2.3
4-cyanothiazole (**3.6**)	1452-15-9	cr	294.1 ± 1.0	146	2.6	3.3
thiophene (**3.7**)	110-02-1	l	115.4 ± 0.6	118,147; 48	1.0	-0.4
4-methylthiazole (**3.8**)	693-95-8	l	112.1 ± 0.8	146	-0.5	-1.4
2-methylthiophene (**3.9**)	554-14-3	l	83.6 ± 0.9	148; 48	1.3	0.3
benzothiazole (**3.10**)	95-16-9	l	203.5 ± 1.0	76,149; 76,149,150	-2.9	-3.5
2,2'-dithiophene (**3.11**)	492-97-7	cr	247.5 ± 2.7	151	-1.7	-3.1
benzo[b]thiophene (**3.12**)	95-15-8	cr	168.2 ± 1.0	56; 152: 153,154	1.5	0.8
2,5-dimethylbenzothiazole (**3.13**)	95-26-1	cr	120.4 ± 2.5	76	2.6	2.7
dibenzothiophene (**3.14**)	132-65-0	cr	213.7 ± 1.5	56,155: 156 ; 134,155: 154	-0.9	-1.5
			Testing set			
2,2'-disulfanediyldianiline (**3.15**)	1141-88-4	cr	226.0 ± 4.3	58	2.0	4.9
4,4'-disulfanediyldianiline (**3.16**)	722-27-0	cr	240.5 ± 5.1	58	7.4	8.0
3-methylthiophene (**3.17**)	616-44-4	l	82.9 ± 0.9	157; 48,157	1.7	0.8
2-benzothiazolamine (**3.18**)	136-95-8	cr	179.8 ± 1.9	91: 95; 91	3.2	2.6
2-methylbenzothiazole (**3.19**)	120-75-2	l	140.5 ± 2.8	76	14.3	14.1
5-fluoro-2-methylbenzothiazole (**3.20**)	399-75-7	l	$-(47.0 \pm 4.3)$	94	9.1	
benzo[b]thiophene-2-carboxylic acid (**3.21**)	6314-28-9	cr	$-(208.6 \pm 3.8)$	96	4.0	3.5
1,2,3,4-tetrahydrodibenzothiophene (**3.22**)	16587-33-0	l	102.0 ± 1.5	158	-0.8	-0.1

[a] Sources of combustion or reaction energies used to derive the condensed-phase $\Delta_f H^\circ_m$ and sources of enthalpies of sublimation or vaporization are separated by semicolon. Unused sources (if any) are listed after colon for each field; [b] $\Delta = \Delta_f H^\circ_m$(calc) - $\Delta_f H^\circ_m$(exp), kJ·mol^{-1}

Table 7: Thermochemical properties of organic compounds with the sulfur double bond, S(IV), and S(VI) at $T = 298$ K

Chemical Name	CASRN	Phase at T	Exp. $\Delta_f H^\circ_m(g)$ / kJ·mol^{-1}	References[a]	Δ(QZ)[b] / kJ·mol^{-1}	Δ(CBS)[b] / kJ·mol^{-1}
		Training set				
thioacetamide (**4.1**)	62-55-5	cr	12.9 ± 1.1	159: 160; 159,160	1.2	2.0
imidazolidine-2-thione (**4.2**)	96-45-7	cr	71.0 ± 2.1	59	−3.3	−3.1
1-aza-2-cycloheptanethione (**4.3**)	7203-96-5	cr	$-(3.5 \pm 2.5)$	60	2.1	4.0
1,3-dihydro-2H-benzimidazole-2-thione (**4.4**)	583-39-1	cr	175.1 ± 2.2	61: 161; 61	−2.8	−3.0
1-methyl-1,3-dihydro-2H-imidazole-2-thione (**4.5**)	60-56-0	cr	116.3 ± 2.3	62	1.8	1.6
dimethyl sulfoxide (**4.6**)	67-68-5	l	$-(150.6 \pm 1.0)$	64,65; 162	−3.1	−2.5
thiacyclopentane 1,1-dioxide (**4.7**)	126-33-0	l[c]	$-(358.3 \pm 1.8)$	66; 66,162,163	−1.0	1.0
		Testing set				
1,3-dihydro-5-methoxy-2H-benzimidazole-2-thione (**4.8**)	37052-78-1	cr	19.6 ± 2.8	62	5.2	5.9
3H-1,3-benzothiazole-2-thione (**4.9**)	149-30-4	cr	205.5 ± 3.3	164: 161; 164	3.4	2.0
5-amino-1,3-dihydro-2H-benzimidazole-2-thione (**4.10**)	2818-66-8	cr	174.6 ± 3.7	62	6.6	6.1
2-thiobarbituric acid (**4.11**)	504-17-6	cr	$-(278.2 \pm 4.5)$	165[d], 93; 165: 166	2.5	3.5

[a] Sources of combustion or reaction energies used to derive the condensed-phase $\Delta_f H^\circ_m$ and sources of enthalpies of sublimation or vaporization are separated by semicolon. Unused sources (if any) are listed after colon for each field; [b] $\Delta = \Delta_f H^\circ_m$(calc) - $\Delta_f H^\circ_m$(exp), kJ·mol^{-1}; [c] supercooled; [d] revised using the NIST Combustion Calorimetry Tool[47]

Table 8: Thermochemical properties of S-containing inorganic compounds at $T = 298$ K

Chemical Name	CASRN	Phase at T	Exp. $\Delta_f H^\circ_m(g)$ / kJ·mol^{-1}	References[a]	Δ(QZ)[b] / kJ·mol^{-1}	Δ(CBS)[b] / kJ·mol^{-1}
hydrogen sulfide (**5.1**)	7783-06-4	g	$-(20.6 \pm 0.5)$	67	-0.1	0.2
sulfur dioxide (**5.2**)	7446-09-5	g	$-(296.8 \pm 0.2)$	67	2.2	3.6
sulfur trioxide (**5.3**)	7446-11-9	l	$-(395.9 \pm 0.7)$	68	-1.2	1.8
sulfuric acid (**5.4**)	7664-93-9	l	$-(732.7 \pm 2.0)$	68	2.7	1.2
hydrogen disulfide (**5.5**)	13465-07-1	l	15.6 ± 1.4	74; 75: 167	0.6	0.8
disulfur monoxide (**5.6**)	20901-21-7	l	$-(56.0 \pm 1.4)$	68	0.3	6.8
octasulfur (**5.7**)	10544-50-0	cr	99.9 ± 0.5	71,72	-2.6	-4.7
carbon oxide sulfide (**5.8**)	463-58-1	g	$-(141.7 \pm 2.0)$	68	0.4	1.2
carbon disulfide (**5.9**)	75-15-0	l	116.7 ± 1.0	68	-0.2	1.0

[a] Sources of combustion or reaction energies used to derive the condensed-phase $\Delta_f H^\circ_m$ and sources of enthalpies of sublimation or vaporization are separated by semicolon. Unused sources (if any) are listed after colon for each field; [b] $\Delta = \Delta_f H^\circ_m$(calc) - $\Delta_f H^\circ_m$(exp), kJ·mol^{-1}

Table 9: Thermochemical properties of problematic compounds at $T = 298$ K

Chemical Name	CASRN	Phase at T	Exp. $\Delta_f H^\circ_m(g)$ / kJ·mol^{-1}	References[a]	Δ(QZ)[b] / kJ·mol^{-1}	Δ(CBS)[b] / kJ·mol^{-1}
Reported after 2013 and included in the testing set (see Tables 6 and 7)						
4,4'-disulfanediyldianiline (**3.16**)	722-27-0	cr	240.5 ± 5.1	58	7.4	8.0
2-methylbenzothiazole (**3.19**)	120-75-2	l	140.5 ± 2.8	76	14.3	14.1
5-fluoro-2-methylbenzothiazole (**3.20**)	399-75-7	l	$-(47.0 \pm 4.3)$	94	9.1	
1,3-dihydro-5-methoxy-2H-benzimidazole-2-thione (**4.8**)	37052-78-1	cr	19.6 ± 2.8	62	5.2	5.9
5-amino-1,3-dihydro-2H-benzimidazole-2-thione (**4.10**)	2818-66-8	cr	174.6 ± 3.7	62	6.6	6.1
Not used in model development						
phenoxathiin (**6.1**)	262-20-4	cr	126.4 ± 1.9	77; 77,168,169	−6.0	−7.3
1,3,5-trithiane (**6.2**)	291-21-4	cr	84.6 ± 2.6	53; 53,54	−8.2	−12.0
1,3-dihydroimidazole-2-thione (**6.3**)	872-35-5	cr	164.9 ± 1.7	63	−31.9	−32.2
dimethyl sulfone (**6.4**)	67-71-0	cr	$-(370.6 \pm 1.7)$	64,78; 79: 81	−8.4	−7.0
dimethyl sulfite (**6.5**)	616-42-2	l	$-(483.3 \pm 2.1)$	82	5.5	5.2
dimethyl sulfate (**6.6**)	77-78-1	l	$-(686.6 \pm 2.1)$	82	−8.4	−8.6
benzenesulfonamide (**6.7**)	98-10-2	cr	$-(208.9 \pm 2.3)$[c]	83	−5.3	−3.6
		cr	$-(231.8 \pm 3.0)$	84; 83	17.6	19.3
thiacyclohexane 1,1-dioxide (**6.8**)	4988-33-4	cr	$-(394.8 \pm 1.5)$	85	−9.8	−6.7

[a] Sources of combustion or reaction energies used to derive the condensed-phase $\Delta_f H^\circ_m$ and sources of enthalpies of sublimation or vaporization are separated by semicolon. Unused sources (if any) are listed after colon for each field; [b] $\Delta = \Delta_f H^\circ_m$(calc) - $\Delta_f H^\circ_m$(exp), kJ·mol^{-1}; [c] revised using the NIST Combustion Calorimetry Tool[47]

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Trade names are provided only to specify procedures adequately and do not imply endorsement by the National Institute of Standards and Technology. Similar products by other manufacturers may be found to work as well or better. The authors declare no competing financial interest.

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Graphical TOC Entry