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Critical evaluation of the enthalpies of formation for fluorinated compounds using experimental data and high-level *ab initio* calculations

Eugene Paulechka, **Andrei Kazakov**
Thermodynamics Research Center, Applied Chemicals and Materials Division, National Institute of Standards and Technology, 325 Broadway, Boulder, CO 80305-3337

Abstract

The *ab initio* method for prediction of the enthalpies of formation for CHON-containing organic compounds proposed earlier (*J. Chem. Theory Comput.* **2018**, *14*, 5920-5932) has been extended to their fluorinated derivatives. A single experimental $\Delta_f H^o{}_m$ is typically available for compounds in this scope. Thus, *a priori* evaluation of the data quality was found to be inefficient despite all available experimental data for C_1—C_3 hydrofluorocarbons and 34 data points for medium-size organofluorine compounds being considered. The training set was derived by analyzing consistency of the experimental and predicted values and removal of outliers. Significant issues in the experimental data, including inconsistency across different laboratories, were identified and potential causes for these problems were discussed. A conservative estimate of uncertainty for the experimental $\Delta_f H^o{}_m$ of organofluorine compounds was proposed.

1. Introduction

Fluorinated organic compounds are an important class of chemicals used in the pharmaceutical industry, agriculture, production of polymers, refrigerants, surfactants, and oil-repellants.[1,2,3] Some of these compounds are also considered pollutants due to their toxicity, bioaccumulation, and contribution to global warming. Knowledge of their thermodynamic properties is critical for industrial applications and development of pollution prevention strategies. In this work, we focus on evaluation of their ideal-gas enthalpies of formation, a property essential to process modeling in a variety of applications.

The experimental methods used to determine enthalpies of formation for the compounds of interest include oxygen and fluorine combustion calorimetries, reaction calorimetry, primarily, with alkali metals and hydrogen, and mass spectrometry. Some enthalpies of formation were also derived from complex thermodynamic cycles involving different types of measurements.

As demonstrated below, oxygen combustion calorimetry is the most reliable and widespread method for determination of $\Delta_f H^o{}_m$ for the considered compounds. Two principal techniques

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yauheni.paulechka@nist.gov; andrei.kazakov@nist.gov.

The authors declare no competing financial interest.

have been used in combustion calorimetry. The most popular one involves combustion in a rotating bomb, in which a certain amount of water has been added.[4,5] To use this approach, the studied or auxiliary compound should have sufficient hydrogen content to yield aqueous HF as a main fluorine product. In the second technique, the combustion is performed in a bomb with no water added.[6] This approach has been used for fluorocarbons. To our knowledge, presently, combustion calorimetry measurements for fluorinated compounds are only conducted at the Center of Chemical Research at the University of Porto. The number of fluorinated compounds containing, C, H, O, or N atoms, for which experimental enthalpies of formation have been determined, is well below 200.

The combustion calorimetry experiments are conducted at a high pressure of oxygen (around 3 MPa). A multi-step procedure[4] is used to transform the experimental combustion energies into the standard-state energies of combustion at $T = 298.15$ K. To derive $\Delta_f H^o{}_m$, the reference enthalpies of formation for water, CO_2, and HF(aq) are required. One should note that values for the suggested enthalpy of formation for the latter evolved significantly over time, and the latest recommendations are to a large extent based on the results of Johnson et al.[7,8] Consequently, the results reported in the literature need to be reevaluated with the use of updated reference values.

Another challenge of the method is that the combustion energies of organofluorine compounds are significantly lower than those of the non-fluorinated counterparts. Thus, the calorimetric results are highly sensitive to the incompletely fluorinated impurities.[4] In many cases, the resulting values are based on the results of chemical analyses of products for HF, CO_2, HNO_3, and less frequently for CF_4 and F_2, which adds complexity to the procedure. As demonstrated below, consistency of the results for different laboratories and repeatability-based uncertainties are often worse than those for CHON compounds. All factors listed above make a reliable predictive procedure highly desirable. The existing approaches involving high-level *ab initio* calculations are mostly focused on small (C_1 and C_2) molecules (e.g., Refs. 9, 10).

Historically, the main contributors to the field are

- Thermodynamics Laboratory of the Bartesville Petroleum Research Center, Bureau of Mines (Bartesville, OK, U.S.A.);
- Chemical Thermodynamics Group of the National Chemical Laboratory (Teddington, U.K.)
- Thermochemistry Laboratory of the Moscow State University (Soviet Union);
- Department of Chemistry, University of Porto (Portugal);
- Institute of Organic Chemistry and Biochemistry at the University of Freiburg (Germany);
- Department of Chemistry, University of Windsor (Canada).

Some reliable values originate from the Chemistry Departments of the University of Wisconsin and the Rice University, the National Bureau of Standards (now NIST), the Argonne National Laboratory, and Thermal Research Laboratory of the Dow Chemical

Company (all U.S.A). For brevity, the laboratories will be referred to by location in our discussion (e.g., the Moscow lab).

The goal of this work is to extend the *ab initio* method we proposed earlier[11,12] to organofluorine compounds and evaluate the reliability of the predicted and available experimental gas-phase enthalpies of formation for these compounds.

2. Calculations

We considered conformational equilibria in the studied compounds because, in our previous work, they were shown to have a significant effect even for some moderate-size molecules.[12] The model was adopted that assumed 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 model as was used for the thermal correction to the enthalpy, $\Delta_0^T H$, term. Enthalpy of formation of a given compound was computed as the Gibbs-energy average for the conformer population. The generation of conformers was performed as described earlier.[13,14,15,16] An initial pool of conformer candidates was produced via systematic search using molecular mechanics based on the MMFF94 force field.[17] The resulting conformer candidates were further optimized, and their vibrational spectra were computed with B3LYP/def2-TZVP-D3(BJ).[18,19,20,21] This combination is expected to provide a compromise between computational cost and accuracy for complex molecules.[12] The final set of conformers was established by eliminating duplicated structures and transition states identified from the vibrational analysis. The frequencies were scaled by 0.990 for zero-point vibrational energies (ZPVE). In the “rigid rotor – harmonic oscillator” calculations of the thermal correction $\Delta_0{}^T H$, the scaling factors of 0.96 for hydrogen stretches and 0.985 for all other modes were applied. The rotational symmetry numbers needed for the entropy evaluation were obtained using the libmsym library.[22] The conformer geometries for the single-point energy calculations were optimized with the density-fitted (resolution-of-identity) second-order Møller-Plesset perturbation theory (DF-MP2) with the aug-cc-pvqz basis set.[23,24] Single-point energy calculations were conducted with the 2016 version of local CCSD(T) by Kállay et al.[25,26,27] and the aug-cc-pvqz basis set. DFT calculations were performed with Gaussian 09[28], local CCSD(T) was carried out with MRCC (release of September 25, 2017)[27], and DF-MP2 was done with Psi4 v1.1.[29] The choice of computational tools was motivated by the performance of the methods on the hardware used.[12]

The enthalpies of formation at $T = 298.15$ K were evaluated as[12]:

$$\Delta_f H^\circ = E + \mathrm{ZPVE} + \Delta_0^T H - \sum_{\mathrm{types}} n_i h_i \qquad (1)$$

where E is the total electronic energy from the single-point calculations, ZPVE is the zero-point vibrational energy, and $\Delta_0^T H$ is the thermal correction from 0 to 298.15 K. The effective enthalpies, h_i in eq 1, for C, H, O, and N atomic types where fixed to the values determined in the previous study[12]: 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

$^{-1}$, and $h(\mathrm{N}) = -143612.32$ kJ·mol^{-1}. Determination of the contribution $h(\mathrm{F})$ is one of the goals of the present study. The $h(\mathrm{F})$ values for individual compounds were determined from eq 1 using their experimental $\Delta_f H^o{}_m$, and the final recommendation was derived via averaging of the individual values over the selected training set of molecules.

Reported uncertainties are the expanded uncertainties for a 0.95 level of confidence ($k \approx 2$). For the experimental works, these are based on the authors' uncertainty estimates (mainly repeatabilities) and uncertainties in the reference values.

3. Results

3.1. Experimental data

The enthalpies of formation considered in this work were derived using the original experimental data, reference enthalpies of formation presented in Table 1, and $\Delta_f H(\mathrm{HF(aq)})$ from Johnson et al.[7] shifted by 0.33 kJ·mol^{-1}, as recommended by CODATA.[8] The enthalpies of formation for hydrofluorocarbons are often determined from their enthalpies of combustion which are, in turn, based on the results of chemical analysis for CO_2 and HF. If the average values based on those two analyses differed by more than 4 kJ·mol^{-1} and could not be explained by formation of CF_4, the enthalpy of formation was calculated from the results based on the CO_2 determination, since the latter was suggested to be more reliable.[30] The heat capacities of compounds required to reduce the experimental $\Delta_r H$ to $T = 298.15$ K were taken from NIST ThermoData Engine v.10.3 [31] unless specified otherwise.

When fluorinated organic compounds are burnt in oxygen, CF_4 sometimes appears as a product, and larger fluorine content results in a higher yield of CF_4. Consequently, the enthalpy of formation of tetrafluoromethane is an important reference quantity affecting experimental $\Delta_f H^o{}_m$ for many compounds. The enthalpy of formation $\Delta_f H^o{}_m = -(933.2 \pm 0.8)$ kJ·mol^{-1} [32] was derived by Greenberg and Hubbard from the experiments on graphite combustion in fluorine. The values obtained by Domalski and Armstrong using a similar technique[37] and in references therein are consistent with this result. On the other hand, the enthalpy of reaction $CF_4(g) + 2H_2O = CO_2(g) + 4HF(\cdot 20H_2O)$, $\Delta_r H^o{}_m = -(173.2 \pm 1.3)$ kJ·mol^{-1} [38,39,40], can be derived from the results of experiments in which poly(tetrafluoroethylene) and perfluorobicyclohexyl were burnt in oxygen with some water present. This value implies $\Delta_f H^o{}_m = -(936.2 \pm 2.9)$ kJ·mol^{-1} for CF_4, if the reference data above are used. The difference between this value and the direct result[32] is relatively large, although the corresponding error bars slightly overlap. The apparent inconsistency should be resolved by replacing the enthalpy of formation of either CF_4 or HF(aq) (or both) with more accurate value(s). In the current Active Thermochemical Tables[36], the statistical analysis yielded $\Delta_f H^o{}_m(\mathrm{HF \cdot 20H_2O}) = -(321.03 \pm 0.16)$ kJ·mol^{-1}, which is 0.86 kJ·mol^{-1} less negative than the CODATA value. On the other hand, Ganyecz et al.[41] computationally analyzed the thermochemical network for fluorinated and chlorinated methanes and ethanes using the diet-HEAT-F12 protocol[42] and concluded that $\Delta_f H^o{}_m(CF_4)$ by Greenberg and Hubbard is not consistent with the *ab initio* results and needs further studies. Overall, the CODATA $\Delta_f H^o{}_m(\mathrm{HF(aq)})$ is supported by a larger number of experimental studies as compared to that for $\Delta_f H^o{}_m(CF_4)$, but it is still insufficient to make a conclusive assessment.

In this work, we used $\Delta_f H^o_m(CF_4) = -(933.2 \pm 0.8)$ kJ·mol^{-1} if CF_4 was one of the major combustion products. If a small amount of CF_4 was formed and reduction of the experimental data implied its hydrolysis, the enthalpy change $\Delta_r H^o_m = -(173.2 \pm 1.3)$ kJ·mol^{-1} was used.

Fluorinated organic compounds, for which the enthalpies of formation are available, can be tentatively divided into three groups. The first group consists of relatively large molecules typically containing more than five carbon atoms. This group has been most studied over the past decades. The second group includes small (up to three carbon atoms) hydrofluorocarbons, most of which are gases at ambient conditions. The third group consists of inorganic species such as HF or NF_3. In this work, 22 compounds (34 $\Delta_f H^o_m$ values) from group 1 (Table 2) were selected to provide reasonable variability with respect to the molecular structural features and the sources of information (i.e., the labs where the measurements were performed). Consideration of the data origins was important to avoid any bias due to a potential systematic error originating from a laboratory. The best effort was made to provide a comprehensive review of the experimental data for small hydrofluorocarbons (Table 3). The considered inorganic species included F_2, HF, OF_2, and NF_3.

For all compounds from the first group (Table 2), the enthalpies of formation were derived from their energies of combustion in oxygen in a rotating bomb calorimeter. In most cases, the well-established technique of combustion in the presence of water[4,5] was used. A detailed discussion of these results is presented below.

Multiple experimental techniques, including oxygen and fluorine combustion calorimetry, reaction calorimety with alkaline metals and hydrogen, chemical equilibrium studies, and mass spectrometry were used to obtain $\Delta_f H^o_m$ for small hydrofluorocarbons.

Fluoromethanes.—Enthalpies of formation for difluoromethane and trifluoromethane were determined by Neugebauer and Margrave[76] from the results of combustion calorimetry. The recommended $\Delta_f H^o_m$ of CF_4 is based on the results of direct combustion of graphite in fluorine.[32]

1,1-Difluoroethane.—The enthalpy of formation was reported by Kolesov et al.[77] The authors analyzed the CO_2 and HF content in the combustion products. The enthalpies of combustion based on these two values differed by about 13 kJ·mol^{-1}. The enthalpy of combustion accepted in this paper was calculated from the CO_2 analysis.

1,1,1-Trifluoroethane.—The enthalpy of formation was determined by Kolesov et al.[78] from the results of combustion calorimetry. Later, Kolesov and Papina[79] revised the experimental value by adding a correction for reduction to the standard state missing in the original work. Analysis of the kinetic data by Rodgers and Ford[101] provides a similar value if $\Delta_f H(CH_3)$ and $\Delta_f H(CF_3)$ from Ref. 35 are used. However, the expanded uncertainty exceeds 10 kJ·mol^{-1} in this case.

1,1,2-Trifluoroethane.—The enthalpy of formation was calculated from the enthalpies of chlorotrifluoroethylene hydrogenation $\Delta_r H^o{}_m$(298 K) = −(271.2 ± 2.3) kJ·mol^{-1} [83] and its enthalpy of formation $\Delta_f H^o{}_m(CF_2CFCl)$ = −(517.1 ± 2.2) kJ·mol^{-1} found as weight-average of the results from Refs. 80,81,82.

Pentafluoroethane.—The enthalpy of formation was reported by Buckley et al.[102] who studied chemical equilibria:

$CF_3CF_2Br(g) + I_2(g) = CF_3CF_2I(g) + IBr(g)$

$Br_2(g) + C_2F_5H(g) = HBr(g) + CF_3CF_2Br(g)$

The equilibrium constants for the second reaction were determined by Coomber and Whittle.[103] However, the reported $\Delta_f H^o{}_m(CF_3CF_2H)$ was, in turn, based on $\Delta_f H^o{}_m(CF_3CF_2I)$ estimated by Wu et al.[104] as $\Delta_f H^o{}_m(CF_3CF_2I) = ½(\Delta_f H^o{}_m(CF_3CF_3) + \Delta_f H^o{}_m(CF_2ICF_2I))$. Thus, this compound was excluded from further data analysis.

Hexafluoroethane.—The most precise value was obtained by Sinke[85] by the reaction bomb calorimetry. The result strongly depends on reference $\Delta_f H^o{}_m$ of CF_4 and NF_3.

1-fluoropropane, 2-fluoropropane, 2,2-difluoropropane.—The enthalpies of formation for monofluoropropanes were obtained using the high-temperature enthalpies of hydrogenation determined in a flow calorimeter by Lacher et al.[86] Enthalpies of the formal reactions

$CH_2{=}CHF + CH_4 = CH_3CHFCH_3$

$CH_2{=}CF_2 + CH_4 = CH_3CF_2CH_3$

could be found from results of the mass-spectrometric study.[87]

1,1,1,3,3,3-Hexafluoropropane.—The enthalpy of combustion and formation for this compound was reported by Kolesov.[88] The concentration of the resulting HF solution was not specified. In the review[89], the enthalpy of formation was recalculated with respect to the updated enthalpies of formation for the reference compounds.

Octafluoropropane.—$\Delta_f H^o{}_m$ was found[90] from the enthalpy of its reaction with sodium. Detailed analysis of the combustion products was performed.

Fluoroethylene, 1,1-difluoroethylene, trifluoroethylene.—Kolesov et al. conducted combustion calorimetry studies for these compounds.[30,92] $\Delta_f H^o{}_m$ of 1,1-difluoroethylene was also reported by Neugebauer and Margrave.[91]

Tetrafluoroethylene.—The enthalpy of formation for this compound was reported by many researchers. Neugebauer and Margrave[91] and Kolesov et al.[95] measured the energy of combustion for the amorphous carbon product.

Equilibria of mono- and difluoropropenes.—We are aware of two works reporting these equilibria.[96,97] While the enthalpies of *Z/E*-isomerization of 1-propenes are consistent, the enthalpies of formation for 3-fluoropropene differ by 8 $kJ·mol^{-1}$. That cannot be explained by their temperature difference.

3,3,3-Trifluoropropene.—The enthalpy of formation for this compound was determined[98] from its enthalpy of combustion in oxygen in a bomb calorimeter. The average values of the enthalpy of combustion derived from the results of chemical analysis for HF and CO_2 differ by about 5 $kJ·mol^{-1}$. The enthalpy of formation was recalculated based on the amount of CO_2. The $\Delta_f H^o_m$ values obtained in experiments 1 and 3 of the original publication are over 20 $kJ·mol^{-1}$ too high relative to the other experiments, while the standard deviation calculated for experiments 2 and (4 to 12) is only 1.7 $kJ·mol^{-1}$. Thus, the enthalpy of formation was calculated using the data from experiments 2 and 4 to 12.

Hexafluoropropene.—Following Papina and Kolesov[99], the enthalpy of formation for this compound can be determined using the enthalpies of the processes

$CF_2ClCFClCF_3(l) + O_2(g) + 4H_2O(l) = 3CO_2(g) + 6HF(·20H_2O) + 2HCl(·600H_2O)$
$\Delta H_m{}^o(298\ K) = -(925.6 \pm 2.0)\ kJ·mol^{-1}$ [99]

$CF_3CF{=}CF_2(g) + Cl_2(g) = CF_2ClCFClCF_3(g)\ \Delta_r H_m{}^o(363\ K) = -(197.3 \pm 0.5)\ kJ·mol^{-1}$ [100]

$CF_2ClCFClCF_3(l) = CF_2ClCFClCF_3(g)\ \Delta_l{}^g H_m{}^o(298\ K) = (26.93 \pm 0.03)\ kJ·mol^{-1}$ [105]

The temperature dependence of $\Delta_r H_m{}^o$ for the chlorination reaction can be neglected.

The enthalpy of reaction

$C_2F_4(g) = 2/3\ CF_3CF{=}CF_2(g)\ \Delta_r H_m{}^o(298\ K) = -86\ kJ·mol^{-1}$

was estimated by Duus[94] using combustion experiments.

Four inorganic compounds were considered: F_2, HF, NF_3, and OF_2. The enthalpies of formation of HF and NF_3 are given in Table 1, for OF_2, $\Delta_f H^o_m = (24.5 \pm 1.6)\ kJ·mol^{-1}$.[106]

3.2. Consistency of experimental data and derivation of the training set

For generation of the CHON training set[11], we used only those compounds for which the experimental data were available from multiple consistent sources and the resulting expanded uncertainty was under 2 $kJ·mol^{-1}$. If these criteria were applied to the fluorinated compounds, a training set of sufficient size could not be compiled. Thus, all available data were analyzed. The effective enthalpy of fluorine, *h*(F), was derived for each data point using eq 1 and the experimental $\Delta_f H^o_m$. The resulting *h*(F) were used to assess the consistency among the considered data points and identification of outliers.

The effective enthalpies *h*(F) for the compounds of group 1 are compared in Figure 1. The value *h*(F) = −261711.5 $kJ·mol^{-1}$ used in the figure is a preliminary estimate based on all available experimental data. Most of the data are spread within (−4 to 6) $kJ·mol^{-1}$ of this estimate. One would expect *h*(F) values to congregate near a certain value. This consistency should be better for compounds with similar fluorine functionality (e.g., para-substituted fluorinated benzene derivatives). Considering the uncertainty of the predicted $\Delta_f H^o{}_m$ was (2.5 to 3.0) $kJ \cdot mol^{-1}$ for CHON-containing compounds[12], variations below 1 $kJ \cdot mol^{-1}$ due to computational model limitations are expected.

The results from the Moscow and Teddington labs do demonstrate reasonable consistency. On the other hand, the values from Freiburg exhibit a scatter of about ±6 $kJ \cdot mol^{-1}$ around the average value for this laboratory. These data as well as those from Windsor where a less precise technique was used were excluded from the training set. Four out of six values from the Bartesville lab and five out of nine values from the Porto lab show significant positive deviation from the average. It implies that the experimental $\Delta_f H^o{}_m$ is more negative than the expected computed counterpart. Two reasons may be responsible for the observed behavior. First, the samples could contain incompletely fluorinated impurities. This may also explain why not all results from these laboratories are biased. Second, the reduction to the standard state could be based on obsolete reference values. The samples of 4-fluorobenzoic acid (#16) from the Bartesville lab were further studied in the Teddington lab and at the National Bureau of Standards and (1.5 to 2.3) $kJ \cdot mol^{-1}$ more positive values were obtained. At the same time, the results from these and two other laboratories are consistent within ±0.5 $kJ \cdot mol^{-1}$ (Table 2). The enthalpies of formation for non-fluorinated compounds from the Porto and Bartesville labs are normally consistent with the results from the other laboratories and the predicted values. Thus, it seems highly unlikely that the problem is due to the instrumental error such as incorrect calibration, etc. Further clarification of this problem clearly goes beyond the scope of this paper. All results from these two laboratories exceeding +2 $kJ \cdot mol^{-1}$ deviation were excluded from the training data set. If several consistent $\Delta_f H^o{}_m$ were available for a compound, the weight-average was calculated with the weights determined from uncertainties of the enthalpies of combustion. The resulting values used in the training set are shown in bold in Table 2.

The data scatter for small fluorinated organics (Figure 2) is larger than that for the compounds of group 1, with $\Delta h(\mathrm{F})$ generally within ±9 $kJ \cdot mol^{-1}$. Seven out of twelve saturated compounds are grouped in the range −(0.2 to 2.0) $kJ \cdot mol^{-1}$. Six of these values were obtained from combustion calorimetry and one from reaction calorimetry. Combustion calorimetry was used to derive only one outlying value, where a thermodynamic cycle also involved the results from a high-temperature hydrogen reaction calorimetry. Therefore, for the saturated compounds, combustion calorimetry was the most reliable technique despite all difficulties associated with quantification of the combustion process for gaseous species. Unlike the condensed-phase compounds, the exact amount of a gas introduced to the bomb is unknown and only chemical analysis of the products allows one to determine the burnt amount of the sample.

Five values for the fluorinated alkenes lie close to −4 $kJ \cdot mol^{-1}$. Four of these values are based on the combustion calorimetry results from the Moscow lab. Different methods were used for tetrafluoroethylene ($n = 4$), which is the fifth consistent compound. However, based on the high-level *ab initio* calculations, $\Delta_f H^o{}_m$ of the latter has been demonstrated to have a large error (see, for example, Ref. 9). The combination of this fact with the results in Figure 2 leads to a conclusion that the remaining four experimental values have a similar systematic error *per fluorine atom*. A possible explanation of this problem might be either incorrect characterization of the combustion products or incorrect reduction to the standard state. The value for perfluoropropene is consistent with those of the saturated compounds. This h(F) was derived in a different way: it is based on a thermodynamic cycle involving the results of combustion calorimetry from the Moscow lab and high-temperature chlorination calorimetry.

Based on the analysis above, we selected the consistent experimental $\Delta_f H^o_m$ of the saturated compounds and perfluoropropene for further analysis. The results for inorganic compounds are close to those of small fluorinated alkanes (Figure 2).

3.3. Effective enthalpy of the fluorine atom for ab initio calculations

Data consistency for the training dataset is demonstrated in Figure 3. At a small number of fluorine atoms, the results for group 1 are typically higher than those for group 2. For perfluorinated compounds of group 1 except perfluorobenzene, h(F) values are close to those of group 2. The exact reason of this behavior is unknown; however, based on our limited tests, we believe that this is mainly due to the insufficient theory level for ZPVE calculations.

The resulting **h(F) = −(261711.80 ± 0.37) kJ·mol^{-1}** was found by unweighted averaging all h(F) values. The enthalpies of formation calculated with this effective enthalpy are presented in Tables 2 and 3. The uncertainty (in kJ·mol^{-1}) for compounds can be estimated as follows:

$$U(\Delta_f H^\circ_m) = \sqrt{U^2(\text{CHON}) + (U(h(\text{F}))n(\text{F}))^2} \quad (2)$$

The first term in the right-hand side of eq 2 is a contribution associated with C, H, O, and N atoms, which can be calculated as described earlier.[12] This contribution considers uncertainty of the model as well as uncertainties of the effective enthalpies of atoms. For the considered compounds, U(CHON) is close to (2.5 to 3.0) kJ·mol^{-1}. Eq 2 does not consider uncertainties in the reference enthalpies of formation for CO_2, H_2O, HF(aq), etc. The uncertainty of h(F) could be decreased if repeated consistent measurements for some reference compounds were available, which is unlikely with current experimental infrastructure. Also, predictions could be improved through the development of efficient and reliable computational procedures for anharmonic ZPVE, which appears to be a limiting factor for the considered group of compounds.

4. Conclusion

An *ab initio* method for prediction of the enthalpies of formation has been extended to fluorinated compounds. Additional uncertainty associated with the presence of fluorine was estimated to be about 1 kilojoule per mole per F atom. Analysis of the experimental data with the use of the computed results revealed significant problems in the former. These included systematic errors of $\Delta_f H^o_m$ in some laboratories and a shortage of reliable $\Delta_f H^o_m$ values for fluoroalkenes. The observed agreement between the experimental and computed values was somewhat worse than for CHON compounds. If no additional information is available, 5*n*(F) kJ·mol^{-1} should be considered as a conservative estimate of the expanded uncertainty for the experimental values of $\Delta_f H^o_m$ of medium-size fluorinated organic compounds. For small hydrofluorocarbons, this uncertainty should be close to 9*n*(F) kJ·mol^{-1}.

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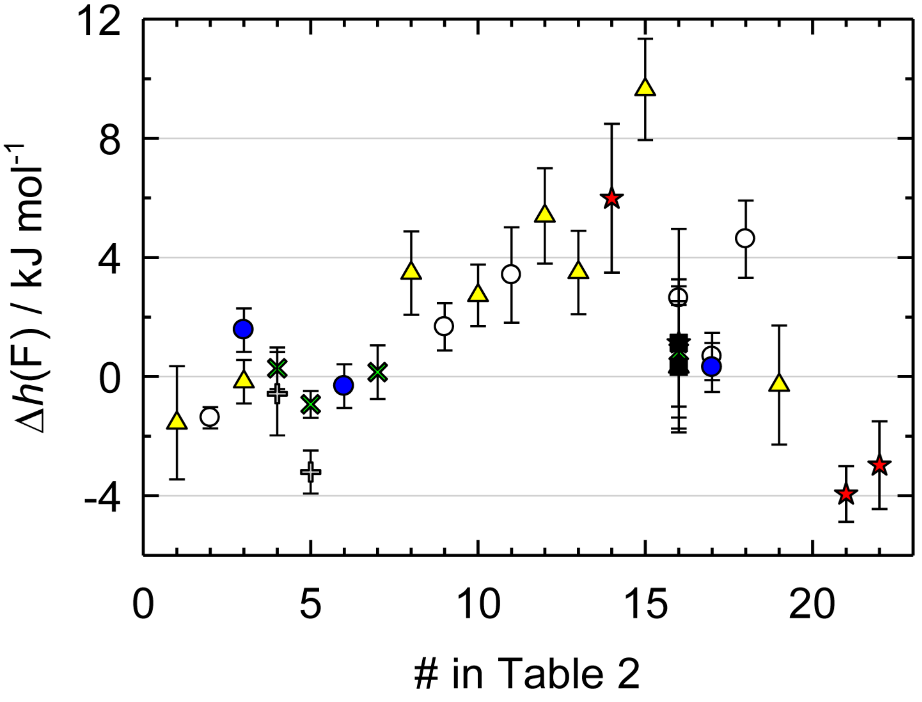

Figure 1.

Relative effective enthalpy, $\Delta h(\mathrm{F})$ / (kJ·mol^{-1}) = $h(\mathrm{F})$ / (kJ·mol^{-1}) + 261711.5, of a fluorine atom for the medium-size organic molecules as a function of the sequential number of a compound in Table 2: blue circles, Moscow lab; yellow triangles, Porto lab (1997-2014); green crosses, Teddington lab; gray pluses, Windsor lab; red stars, Freiburg lab; empty circles, Bartesville; black squares, Gaithersburg. The value for 5-fluoro-2-methylbenzoxazole (#20) is not shown due to a large deviation (−8.6 kJ·mol^{-1}). For 5-fluorouracil (#1) and (trifluoromethyl)benzene (#17) only the most recent values for laboratories are shown.

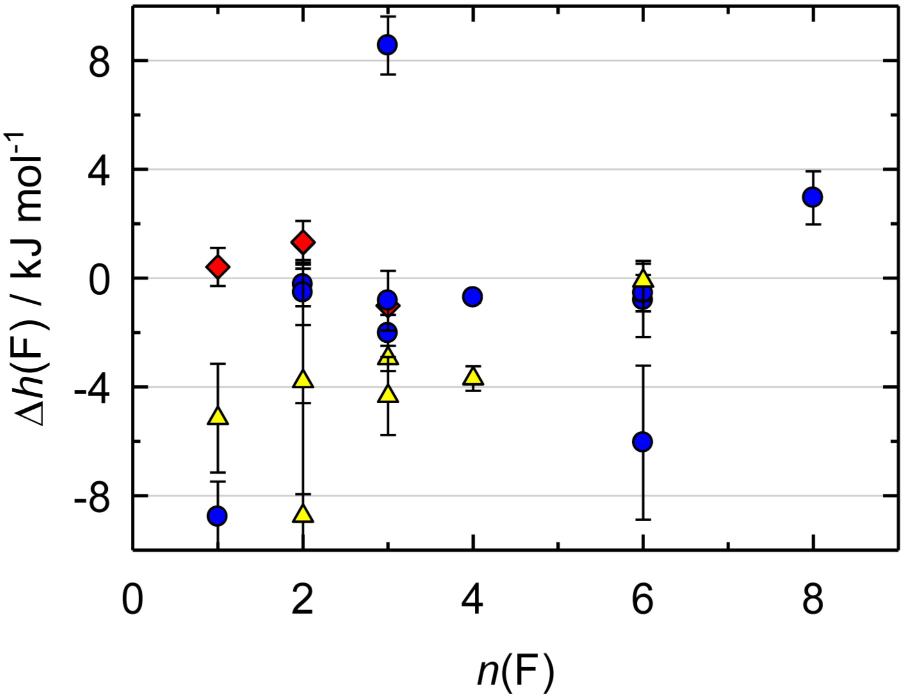

Figure 2.

Relative effective enthalpy, Δh(F) / (kJ·mol^{-1}) = h(F) / (kJ·mol^{-1}) + 261711.5, of a fluorine atom for fluoroalkanes (blue circles), fluoroalkenes (yellow triangles), and inorganic molecules (red diamonds). The value for 2-fluoropropane (−22 kJ·mol^{-1}) is not shown. For tetrafluoroethylene, the value is a weight-average of the results[91,95]

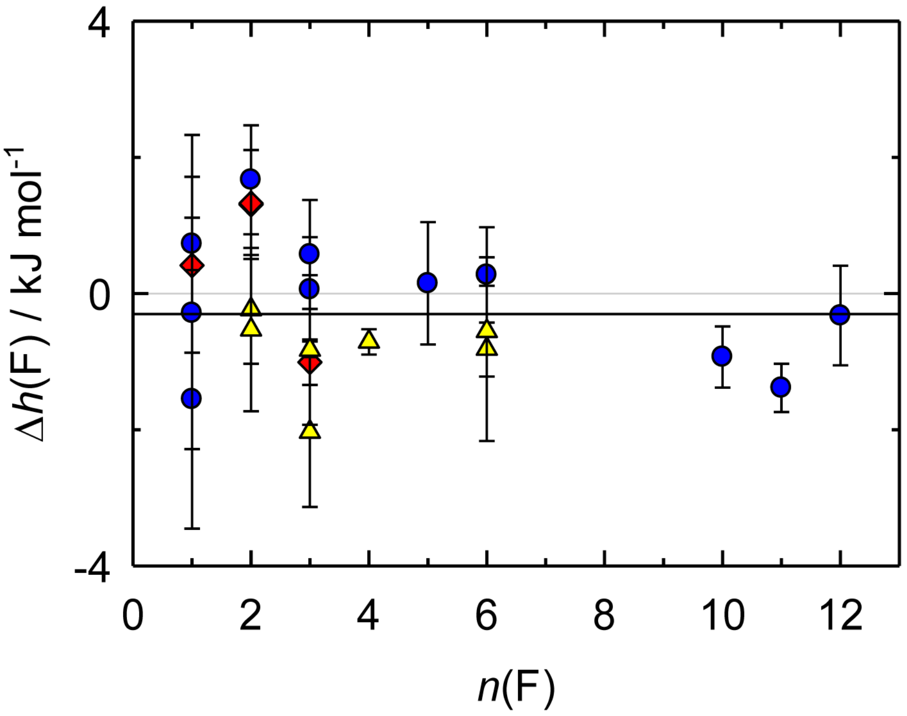

Figure 3.

Relative effective enthalpy, $\Delta h(\mathrm{F})$ / (kJ·mol^{-1}) = $h(\mathrm{F})$ / (kJ·mol^{-1}) + 261711.5, of a fluorine atom for group 1 (blue circles), small hydrofluorocarbons (yellow triangles), and inorganic molecules (red diamonds). The black line shows the resulting $h(\mathrm{F})$ value.

Table 1.

Reference enthalpies of formation used in this work[a]

Compound	$\Delta_f H^o_m$/kJ·mol^{-1}	Reference
CO_2(g)	−393.51 ±0.13	8
H_2O(l)	−285.83 ± 0.04	8
F^-(aq)	−335.35 ± 0.65	8
HF(l)	−303.55 ± 0.25	7
HF(g)	−273.30 ± 0.70	8
HCl(g)	−92.31 ± 0.10	8
CF_4(g)	−933.2 ± 0.8[b]	32
NF_3	−131.5 ± 1.0	33, 34
NaF(cr)	−576.6 ± 0.7	35
KF(cr)	−569.9 ± 0.7	35
NaCl(cr)	−411.26 ± 0.12	35
propane	−104.6 ± 0.2	36

[a] Reported uncertainties are the expanded uncertainties for 0.95 level of confidence

[b] see discussion in the text

Table 2.

Experimental thermochemical data at $T = 298.15$ K for organofluorine compounds composed of medium-size molecules[a]

Compound	**Formula**	**CASRN**	**Phase at *T***	**$\Delta_f H^o_m$(cond) kJ·mol^{-1}**	**$\Delta_{cond}{}^g H^o_m$ kJ·mol^{-1}**	**Lab.[b]**	**Ref.**	**$\Delta_{cond}{}^g C^o_{p,m}$ J·K^{-1}·mol^{-1}**	**$\Delta_f H^o_{m,exp}$ kJ·mol^{-1}**	**$\Delta_f H^o_{m,calc}$ kJ·mol^{-1}**
5-fluorouracil (1)	$C_4H_3FN_2O_2$	51-21-8	cr		132.1 ± 2.8		43	−19[c]		
					153.6 ± 5.0		44			
				−581.9 ± 1.2		A	45			
				−586.8 ± 1.1	131.9 ± 1.8	A	46			
				−586.8 ± 1.1	**132.0 ± 1.5**				**−454.8 ± 1.9**	−456.1
perfluoropiperidine (2)	$C_5F_{11}N$	836-77-1	l	**−2076.2 ± 3.9**	**30.0 ± 0.2**	B	47		**−2046.2 ± 3.9**	−2058.2
(trifluoroacetyl)acetone (3)	$C_5H_5F_3O_2$	367-57-7	l		**37.2 ± 0.2**		48			
				−1039.4 ± 3.3		C	49			
				−1034.2 ± 2.3		A	50			
				−1034.9 ± 2.3					**−997.7 ± 2.3**	−996.6
hexafluorobenzene (4)	C_6F_6	392-56-3	l	−991.1 ± 4.2		D	51			
				−982.7 ± 8.4		E	6			
				−991.1 ± 4.2	**35.6 ± 0.3**[d]				**−955.5 ± 4.2**	−952.1
decafluorocyclohexene (5)	C_6F_{10}	355-75-9	l	−1966.6 ± 4.5	30.8	D	51			
				−1938.0 ± 7.2	31.0	E	52			
				−1966.6 ± 4.5	**30.9 ± 0.1**				**−1935.7 ± 4.5**	−1942.1
perfluoro(2-methyl-2-pentene) (6)	C_6F_{12}	1584-03-8	l	**−2522.4 ± 8.8**[e]	**23.4 ± 0.4**	C	53		**−2499.0 ± 8.8**	−2499.3
pentafluorophenol (7)	C_6HF_5O	771-61-9	cr	−1024.2 ± 4.5	*f*	D	54			
					67.8 ± 0.5		55, 56[g]			
				−1024.2 ± 4.5	**67.8 ± 0.5**				**−956.4 ± 4.5**	−954.2
4-fluoronitrobenzene (8)	$C_6H_4FNO_2$	350-46-9	l	−189.6 ± 1.4	56.0 ± 0.2	A	57		−133.6 ± 1.4	−129.8
1,4-difluorobenzene (9)	$C_6H_4F_2$	540-36-3	l	−342.2 ± 1.6	35.8 ± 0.2[h]	B	58		−306.4 ± 1.6	−302.5
2-trifluoroacetylpyrrole (10)	$C_6H_4F_3NO$	2557-70-2	cr	−776.6 ± 2.8	72.8 ± 1.4	A	59	−50	−703.8 ± 3.1	−694.7
Fluorobenzene (11)	C_6H_5F	462-06-6	l	−150.6 ± 1.6	34.7 ± 0.1[d]	B	40		−115.9 ± 1.6	−112.2

Compound	Formula	CASRN	Phase at T	$\Delta_f H^o_m$(cond) kJ·mol^{-1}	$\Delta_{cond}^g H^o_m$ kJ·mol^{-1}	Lab.[b]	Ref.	$\Delta_{cond}^g C^o_{p,m}$ J·K^{-1}·mol^{-1}	$\Delta_f H^o_{m,exp}$ kJ·mol^{-1}	$\Delta_f H^o_{m,calc}$ kJ·mol^{-1}
4-fluoroaniline (12)	C_6H_6FN	371-40-4	l	−164.0 ± 1.4	54.8 ± 0.8	A	60		−109.2 ± 1.6	−103.5
5-fluoro-1,3-dimethyluracil (13)	$C_6H_7FN_2O_2$	3013-92-1	cr		*121 ± 3*		44			
				−575.0 ± 1.2	96.8 ± 1.6	A	46	−30		
					98.0 ± 0.9		61			
					97.7 ± 0.8				−477.3 ± 1.5	−473.5
fluorocyclohexane (14)	$C_6H_{11}F$	372-46-3	l	−373.5 ± 2.0 [i]	36.9 ± 1.5	F	62	−54[j]	−336.7 ± 2.5	−330.4
4-fluorobenzonitrile (15)	C_7H_4FN	1194-02-1	cr	−53.5 ± 1.6	67.6 ± 0.5	A	63	−25	14.1 ± 1.7	24.0
4-fluorobenzoic acid (16)	$C_7H_5FO_2$	456-22-4	cr	*−586.7 ± 1.6*		B	40			
				−584.9 ± 1.4		D	51			
					93.7 ± 1.7		54	−15[k]		
				−585.2 ± 1.3		G	64			
				−584.4 ± 1.4		G	64			
				−585.2 ± 1.3		F	62			
				−584.4 ± 1.2		A	65			
					92.7 ± 1.6		66			
				−584.8 ± 1.2	**93.1 ± 1.1**				**−491.7 ± 1.6**	−490.7
(trifluoromethyl)benzene (17)	$C_7H_5F_3$	98-08-8	l	−635.0 ± 2.7		B	40			
				−636.9 ± 2.2		B	67			
				−640.6 ± 3.4		C	68			
				−635.8 ± 2.3		C	49			
				−636.6 ± 2.2	**37.9 ± 0.9**[d]				**−598.7 ± 2.4**	−596.1
4-fluoromethylbenzene (18)	C_7H_7F	352-32-9	l	−186.9 ± 1.3		B	58			
					39.4 ± 0.1		69		−147.5 ± 1.3	−142.6
1-fluoro-4-methoxybenzene (19)	C_7H_7FO	459-60-9	l	**−308.9 ± 1.6**	**48.7 ± 1.1**	A	70		**−260.2 ± 2.0**	−260.2
5-fluoro-2-methylbenzoxazole (20)	C_8H_6FNO	701-16-6	l	−260.2 ± 3.8	57.2 ± 1.0	A	71		−203.0 ± 3.9	−211.3
(2,2,2-trifluoroethyl)benzene (21)	$C_8H_7F_3$	21249-93-4	l	−669.0 ± 2.8	46.1 ± 0.5	F	62	*l*	−622.9 ± 2.8	−633.8
1,1'-(1,1,2,2-tetrafluoro-1,2-ethanediyl)bis-benzene (22)	$C_{14}H_{10}F_4$	425-32-1	cr	−783.0 ± 4.6	101.9 ± 3.7	F	62	*l*	−681.1 ± 5.9	−691.8

[a] Standard molar quantities: $\Delta_f H^o_m$(cond), the enthalpy of combustion of a compound in the condensed state; $\Delta_{cond}{}^g H^o_m$, the enthalpy of sublimation or vaporization; $\Delta_{cond}{}^g C^o_{p,m}$, the heat capacity difference between the ideal-gas and condensed phases; $\Delta_f H^o_{m,exp}(g)$ and $\Delta_f H^o_{m,calc}(g)$, the experimental and calculated ideal-gas enthalpies of formation, respectively. All experimental enthalpies of combustion and formation are recalculated using the reference values from Table 1. Values selected for generation of the training data set are given in bold; the values not used for averaging are italicized. Reported uncertainties are the expanded uncertainties for 0.95 level of confidence

[b] Source of the condensed-state enthalpy of formation: A, University of Porto; B, Bartesville Petroleum Research Center; C, Moscow State University; D, National Chemical Laboratory, Teddington; E, University of Windsor; F, University of Freiburg; G, National Bureau of Standards, Washington, DC

[c] Refs. 31,72

[d] evaluated by NIST ThermoData Engine[31] based on multiple sources

[e] based on CO_2 analysis

[f] the sublimation pressure data[54] include the solid-to-solid phase transition region and are not used

[g] calorimetric data by Paukov et al.[73] are inconsistent with the publications from the Teddington lab. The latter are used to keep consistency between different properties.

[h] Refs. 31,74

[i] assuming that the reported combustion energies refer to $HF{\cdot}20H_2O$.

[j] $\Delta_{vap}C_p$ estimated by NIST ThermoData Engine[31]

[k] Ref. 75

[l] the correction to $T = 298.15$ K was small compared to the uncertainty and not applied

Table 3.

Experimental thermochemical data for small hydrofluorocarbons in the ideal-gas state[a]

Compound	**CASRN**	**Ref.**	**Lab.**[b]	**Reaction**	***T* / K**	**$\Delta_r H^o_m(T)$**	**$\Delta_f H^o_{m,exp}$** [c]	**$\Delta_f H^o_{m,calc}$** [c]
						kJ·mol⁻¹	**kJ·mol⁻¹**	**kJ·mol⁻¹**
CH_2F_2	75-10-5	76	A	$CH_2F_2(g) + O_2(g) = CO_2(g) + 2HF(\cdot 22H_2O)$	298.15	−585.1 ± 0.9	**−452.3 ± 1.6**	−452.2
CHF_3	75-46-7	76	A	$CHF_3(g) + 1/2O_2(g) + H_2O(l) = CO_2(g) + 3HF(\cdot 24H_2O)$	298.15		**−696.6 ± 3.3**	−698.2
CF_4	75-73-0	32	B	$C(gr) + 2F_2(g) = CF_4(g)$	298.15	−933.2 ± 0.8	**−933.2 ± 0.8**	−934.9
CHF_2CH_3	75-37-6	77	C	$C_2H_4F_2(g) + 5/2\ O_2(g) = 2CO_2(g) + H_2O(l) + 2HF(\cdot 20H_2O)$	298.15	−1212.6 ± 2.0	**−504.0 ± 2.4**	−504.5
CF_3CH_3	420-46-2	78, 79	C	$CF_3CH_3 + 2O_2 = 2CO_2 + 3HF(\cdot 27H_2O)$	298.15	−1004.2 ± 2.6	**−748.6 ± 3.3**	−753.8
CHF_2CH_2F	430-66-0	80, 81, 82, 83	C,D	Multiple reactions involving CF_2=CFCl	298.15		−696.0 ± 3.2	−669.5
CF_3CF_2H	354-33-6			See text				−1115.2
CF_3CF_3	76-16-4	84	E	$C_2F_6(g) + 6K = 2C(soot) + 6KF$	298.15	−2088	−1311 ± 17[d]	
		85	F	$C_2F_6 + 2/3NF_3 = 2CF_4 + 1/3N_2$	298.15	−434.7 ± 2.5	**−1344.0 ± 3.0**	−1345.5
$CH_2FCH_2CH_3$	460-13-9	86	D	$C_3H_7F(g) + H_2 = C_3H_8(g) + HF(g)$	521	−95.2 ± 1.0	−284.8 ± 1.3	−293.3
CH_3CHFCH_3	420-26-8	86	D	$C_3H_7F(g) + H_2 = C_3H_8(g) + HF(g)$	521	−88.3 ± 0.7	−292.2 ± 1.1	−313.9
		87	G	$CH_2=CHF(g) + CH_4(g) = C_3H_7F(g)$	298.15	−112.9 ± 6.1		
$CH_3CF_2CH_3$	420-45-1	87	G	$CH_2=CF_2(g) + CH_4(g) = CH_3CF_2CH_3(g)$	298.15	−123.5 ± 6.1		−554.6
$CF_3CH_2CF_3$	690-39-1	88,89	C	$C_3H_2F_6(g) + 2O_2(g) + 2H_2O(l) = 3CO_2(g) + 6HF(aq)$	298.15		−1406.1 ± 8.1	−1409.2
$CF_3CF_2CF_3$	76-19-7	90	C	$C_3F_8(g) + 8Na(cr) = 8NaF(cr) + 3C(amorph)$	298.15	−2761.3 ± 4.9	−1783.7 ± 7.8 [i]	−1757.7
$HFC=CH_2$	75-02-5	30	C	$C_2H_3F(g) + 5/2O_2(g) = 2CO_2(g) + H_2O(l) + HF(\cdot 40H_2O)$	298.15	−1256.1 ± 1.9	−138.7 +± 2.0	−143.6
$F_2C=CH_2$	75-38-7	91	A	$C_2H_2F_2(g) + 2O_2(g) = 2CO_2(g) + 2HF(\cdot 50H_2O)$	298.15	−1096.9 ± 7.0	−334.2 ± 7.1	−351.1
		92	C	$C_2H_2F_2(g) + 2O_2(g) = 2CO_2(g) + 2HF(\cdot 30H_2O)$	298.15	−1086.8 ± 8.2	−344.1 ± 8.3	
$F_2C=CHF$	359-11-5	92	C	$C_2HF_3(g) + 3/2O_2(g) = 2CO_2(g) + 3HF(\cdot 30H_2O)$	298.15	−980.5 ± 3.9	−486.5 ± 4.3	−498.6
$F_2C=CF_2$	116-14-3	84	E	$C_2F_4(g) + 4K = 2C(soot) + 4KF(cr)$	298.15		−706 ± 8[d]	−673.0
		93	H	$C_2F_4(g) + 4K = 2C(gr) + 4KF(cr)$	298.15		−715 ± 11[e]	
		94	I	$C_2F_4(g) = C(soot) + CF_4(g)$	297.31	−257.0 ± 6.4	−676.2 ± 6.5[e]	

Compound	CASRN	Ref.	Lab.[b]	Reaction	T / K	$\Delta_r H^o_m(T)$ kJ·mol^{-1}	$\Delta_f H^o_{m,exp}$ [c] kJ·mol^{-1}	$\Delta_f H^o_{m,calc}$ [c] kJ·mol^{-1}
		94	I	$C_2F_4(g) + 2H_2(g) = 2C(soot) + 4HF(l)$	297.16	−555.3 ± 5.6	−658.9 ± 5.7[e]	
		91	A	$C_2F_4(g) + 2H_2(g) = 2C(amorph) + 4HF(\cdot 18H_2O)$	298.15	−618.1 ± 4.5	−657.0 ± 5.4[f]	
		91	A	$C_2F_4(g) = C(amorph) + CF_4(g)$	298.15	−266.0 ± 1.6	−659.5 ± 2.0[g]	
		95	C	$C_2F_4(g) + 4Na = 2C(amorph) + 4NaF(cr)$	298.15	−1611.3 ± 5.3	−662.1 ± 6.0[h]	
$CH_2FCH{=}CH_2$, *E*-$CH_3CH{=}CHF$, *Z*-$CH_3CH{=}CHF$	818-92-820327-65-519184-10-2	96	J	$CH_2FCH{=}CH_2$ = (*Z* and *E*)-$CH_3CH{=}CHF$	484.0	−22.0 ± 3.4		
		97	K	$CH_2FCH{=}CH_2(g)$ = (*Z*)-$CH_3CH{=}CHF(g)$	658.6	−13.6 ± 0.6		
		97	K	$CH_2FCH{=}CH_2(g)$ = (*E*)-$CH_3CH{=}CHF(g)$	658.6	−11.0 ± 0.6		
		96	J	(*E*)-$CH_3CH{=}CHF(g)$ = (*Z*)-$CH_3CH{=}CHF(g)$	470.5	−2.9 ± 0.5		
		97	K	(*E*)-$CH_3CH{=}CHF(g)$ = (*Z*)-$CH_3CH{=}CHF(g)$	658.6	−2.6 ± 0.6		
$CHF_2CH{=}CH_2$, $CH_3CH{=}CF_2$	430-62-6430-63-7	97	K	$CH_3CH{=}CF_2(g) = CHF_2CH{=}CH_2(g)$	672.6	−10.7 ± 1.2		
$CF_3CH{=}CH_2$	677-21-4	98	C	$C_3H_3F_3(g) + 3O_2(g) = 3CO_2(g) + 3HF(\cdot x H_2O)$, $x = 13$ or 45	298.15		−621.7 ± 1.4	−629.7
$CF_3CF{=}CF_2$	116-15-4	99,100	C,D	Multiple reactions involving $CF_3CFClCF_2Cl$			**−1151.8 ± 4.4**	−1150.6
		94	I	$C_2F_4(g) = 2/3\ CF_3CF{=}CF_2(g)$	299	−86 ± 11		

[a] Standard molar quantities: $\Delta_r H^o_m$, the enthalpy of a reaction shown; $\Delta_f H^o_{m,exp}(g)$ and $\Delta_f H^o_{m,calc}(g)$, the experimental and calculated ideal-gas enthalpies of formation, respectively. All experimental enthalpies of combustion and formation are recalculated using the reference values from Table 1. Values used in the training set are shown in bold. Reported uncertainties are the expanded uncertainties for 0.95 level of confidence

[b] A, University of Wisconsin; B, Argonne National Laboratory; C, Moscow State University; D, University of Colorado at Boulder; E, Imperial Chemical Industries; F, Dow Chemical Company; G, California Institute of Technology; H, University of Göttingen; I, E. I. du Pont de Nemours & Co.; J, University of Rhode Island; K, University of Florida

[c] at $T = 298.15$ K

[d] assuming $\Delta_f H^o_m(soot) = 10.5$ kJ·mol^{-1}

[e] assuming $\Delta_f H^o_m(soot) = 0$ kJ·mol^{-1}

[f] $\Delta_f H^o_m(soot) = 6.2$ kJ·mol^{-1} determined experimentally

[g] $\Delta_f H^o_m(soot) = 7.7$ kJ·mol^{-1} determined experimentally

[h] $\Delta_f H^o{}_m$(soot) = 16.5 kJ·mol^{-1} determined experimentally

[i] $\Delta_f H^o{}_m$(soot) = 22.6 kJ·mol^{-1} determined experimentally.