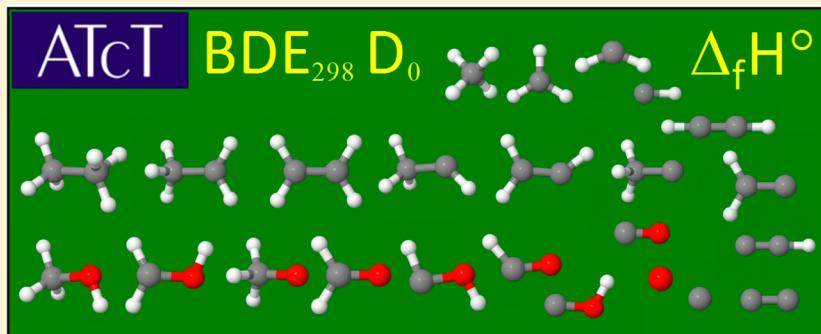


Active Thermochemical Tables: Sequential Bond Dissociation Enthalpies of Methane, Ethane, and Methanol and the Related Thermochemistry

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ABSTRACT: Active Thermochemical Tables (ATcT) thermochemistry for the sequential bond dissociations of methane, ethane, and methanol systems were obtained by analyzing and solving a very large thermochemical network (TN). Values for all possible C–H, C–C, C–O, and O–H bond dissociation enthalpies at 298.15 K (BDE₂₉₈) and bond dissociation energies at 0 K (D₀) are presented. The corresponding ATcT standard gas-phase enthalpies of formation of the resulting CH_n, n = 4–0 species (methane, methyl, methylene, methylidyne, and carbon atom), C₂H_n, n = 6–0 species (ethane, ethyl, ethylene, ethylidene, vinyl, ethylidyne, acetylene, vinylidene, ethynyl, and ethynylene), and COH_n, n = 4–0 species (methanol, hydroxymethyl, methoxy, formaldehyde, hydroxymethylene, formyl, isoformyl, and carbon monoxide) are also presented. The ATcT thermochemistry of carbon dioxide, water, hydroxyl, and carbon, oxygen, and hydrogen atoms is also included, together with the sequential BDEs of CO₂ and H₂O. The provenances of the ATcT enthalpies of formation, which are quite distributed and involve a large number of relevant determinations, are analyzed by variance decomposition and discussed in terms of principal contributions. The underlying reasons for periodic appearances of remarkably low and/or unusually high BDEs, alternating along the dissociation sequences, are analyzed and quantitatively rationalized. The present ATcT results are the most accurate thermochemical values currently available for these species.

INTRODUCTION

Bond dissociation enthalpy (BDE) is one of the most fundamental concepts in chemistry. BDE_T is defined as the change in standard¹ enthalpy at temperature T that occurs upon cleavage of a particular chemical bond, assuming ideal gas behavior of the dissociating chemical species and its dissociation products. BDEs are often colloquially termed bond dissociation energies, even though the quoted quantities invariably refer to enthalpies rather than energies; in most bond ruptures,² the corresponding energy is lower than the quoted enthalpy by RT, R being the gas constant. The two quantities are truly synonymous only in the limit of 0 K, at which point BDE₀ is indeed identical to the 0 K bond dissociation energy, a spectroscopic quantity often denoted as D₀. Thermodynamically, D₀ is defined as the difference in energy between a chemical species and the appropriate dissociation asymptote, where both the reactant and its dissociation products are in their lowest *actually existing* rovibrational energy level of the lowest electronic state.³ For regular chemical species, the lowest

electronic state is obviously the ground electronic state,⁴ although that is not necessarily the case for nonstandard thermochemical species, such as those that are assumed to be thermodynamically equilibrated only within a manifold of electronic states of a particular spin multiplicity—possibly different than the ground-state multiplicity—e.g., singlet methylene, quartet methylidyne, singlet oxygen, etc. (*vide infra*).

BDEs are the most frequently used measures of the strengths of chemical bonds, and detailed knowledge of them has historically led to important new insights on the nature of

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chemical bonding.⁵ Knowledge of accurate enthalpies of formation maps onto knowledge of accurate BDEs, and vice versa, as witnessed by numerous papers where enthalpies of formation (particularly of radicals) are inferred from measured (or accurately computed) BDEs. With few exceptions,⁶ chemical reactions can be thought of as a rearrangement of the chemical bonds of the reactant(s) to form the product(s); the corresponding reaction enthalpy can be formally obtained as the difference between BDEs of the newly formed bonds and those that were broken during the reaction.⁷ Knowledge of accurate BDEs is also important for the development and benchmarking of state-of-the-art electronic structure approaches,⁸ which are now approaching and even exceeding ± 1 kJ/mol accuracies. Last, but most certainly not least, the availability of accurate BDEs and/or enthalpies of formation for a broad range of chemical species is a *sine qua non* for developing realistic chemical models of complex chemical environments, such as combustion or the atmosphere, and is an important motivator for the present study.

Starting from methane, ethane, and methanol, sequential bond dissociations lead to a set of chemical species corresponding to gross formulas CH_n ($n = 4\text{--}0$), C_2H_n ($n = 6\text{--}0$), and COH_n ($n = 4\text{--}0$), as well as OH_n ($n = 1, 0$). Species from these four groups appear as reactants, products, or intermediates in elementary chemical reactions in a variety of environments, ranging from anthropic industrial activities to astrochemistry,⁹ and are hence of substantial general interest in chemistry. In particular, members of these groups of species play significant roles in combustion of even the simplest hydrocarbon fuels^{10–12} and—due to the inherently hierarchical nature of C_n chemical reaction mechanisms¹³—appear as important actors in virtually all combustion mechanisms. The goal of the present contribution is to provide the best currently available values for all possible sequential BDEs of methane, ethane, and methanol, together with the related enthalpies of formation of CH_n (methane, methyl, methylene, methylidyne, and carbon atom), C_2H_n (ethane, ethyl, ethylene, ethylidene, vinyl, ethylidyne, acetylene, vinylidene, ethynyl, and ethynylene), COH_n (methanol, hydroxymethyl, methoxy, formaldehyde, hydroxymethylene, formyl, isoformyl, and carbon monoxide), and OH_n (hydroxyl, oxygen atom) species, as obtained by the Active Thermochemical Tables (ATcT) approach.

METHODS

Active Thermochemical Tables are a novel paradigm in thermochemistry, based on constructing, analyzing, adjusting, and solving a thermochemical network (TN), which contains the known thermochemical interdependencies between the targeted chemical species. Pertinent details of the ATcT approach have been given in some of the earlier papers.^{14–19} Briefly, the ATcT TN is constructed from relevant reaction enthalpies, reaction Gibbs energies, constants of equilibria, adiabatic ionization energies and electron affinities, etc. that were experimentally measured²⁰ or accurately computed. The TN does not incorporate published enthalpies of formations *per se*, because these are normally obtained indirectly²¹ and incorporate additional assumptions about the values of the enthalpies of formation for other chemical species that are involved in the underlying determination. When entered in the TN, each determination is assigned an initial uncertainty that reflects the best estimate of its perceived 95% confidence level.

The TN effectively represents a set of qualified constraints that must be satisfied by the resulting enthalpies of formation. Before obtaining the solutions, ATcT subjects the TN to an analysis that exploits the internally available thermochemical cycles and evaluates each determination and its associated uncertainty for consistency, producing a ranked list of potential “offenders” (determinations with too optimistic initial uncertainties). The uncertainties of these “offenders” are iteratively augmented by a small increment, and the statistical analysis is repeated until internal consistency is achieved across the entire TN. At this point ATcT proceeds to obtain the final set of enthalpies of formation by simultaneously satisfying all interdependences in the TN.

The TN approach allows ATcT to optimally exploit the cumulative knowledge stored in the TN and, perhaps just as important, to dynamically incorporate new measurements when they become available. As a consequence of the TN approach, ATcT produces thermochemical values that possess superior accuracy and robustness when compared to their counterparts obtained by traditional sequential thermochemistry. With respect to the expression of accuracy, ATcT fully follows the standard convention in thermochemistry of providing uncertainties that encompass both trueness and precision and represent earnest estimates of the corresponding 95% confidence intervals.⁸ As long as the uncertainties follow the same standard of expression, the achieved accuracies are easily compared. As a cursory illustration of the overall improvement in accuracy, a comparison with the CODATA²² compilation (which critically evaluated the thermochemistry of a carefully selected small set of “key” species, the recommended values for which were subsequently adopted by virtually all other compilations, such as JANAF²³ and Gurvich et al.²⁴) reveals that the recently published¹⁹ ATcT enthalpy of formation of O atom is ~ 48 times more accurate, N atom is ~ 17 times more accurate, HF is ~ 13 times more accurate, CO_2 is ~ 9 times more accurate, C atom is ~ 8 times more accurate, and even H_2O is ~ 1.5 times more accurate. In contrast to the improvement in accuracy, which is formally expressed through the attached uncertainty, the improvement in the robustness of an enthalpy of formation is less obvious, and relates to the breadth of its provenance. Enhanced robustness of the ATcT enthalpies of formation implicates a higher degree of resilience to a significant change when one of the relevant determinations is removed from consideration. In traditional sequential thermochemistry, the provenance of an enthalpy of formation can be traced back with relative ease, and in the vast majority of cases the quoted value and its attached uncertainty depend on one or more auxiliary enthalpies of formation but were otherwise derived either from a single determination (presumably critically evaluated as being the best available) or—less frequently—as an average of a couple of similar determinations. Clearly, if the provenance is limited, removal of the critical determination will cause the enthalpy of formation of the target species to change significantly or even become undefined, with a detrimental cascading effect on the thermochemistry of other sequentially dependent species. In contrast to this, a typical ATcT enthalpy of formation has a highly distributed provenance and thus tends not to depend critically on the accuracy and reliability of any single determination. In fact, if and when the ATcT enthalpy of formation of a particular species does display a strong dependency on a single thermochemical determination, the latter qualifies as a “weak link”, and the corresponding section

Table 1. Sequential Bond Dissociation Enthalpies of Methane (kJ/mol)

Species	Dissociating Bond ^a	0 K	298.15 K	Uncert.
Methane, CH ₄	H–CH ₃	432.373	438.892	± 0.065
Methyl, CH ₃	H–CH ₂ (to ⁰ CH ₂)	457.21	463.14	± 0.13
	H–CH ₂ (to ³ CH ₂)	457.21	463.14	± 0.13
	H–CH ₂ (to ¹ CH ₂)	494.87	500.66	± 0.13
Methylene (equilib.), ^{eq} CH ₂	H–CH (to ^{eq} CH)	417.86	422.60	± 0.12
	H–CH (to ² CH)	417.86	422.60	± 0.12
	H–CH (to ⁴ CH)	489.62	494.36	± 0.60
Methylene (triplet), ³ CH ₂	H–CH (to ^{eq} CH)	417.86	422.60	± 0.12
	H–CH (to ² CH)	417.86	422.60	± 0.12
	H–CH (to ⁴ CH)	489.62	494.36	± 0.60
Methylene (singlet), ¹ CH ₂	H–CH (to ^{eq} CH)	380.20	385.08	± 0.13
	H–CH (to ² CH)	380.20	385.08	± 0.13
	H–CH (to ⁴ CH)	451.96	456.84	± 0.60
Methylidyne (equilib.), ^{eq} CH	C–H (to ^{eq} C)	334.65	338.77	± 0.10
	C–H (to ³ C)	334.65	338.77	± 0.10
	C–H (to ¹ C)	456.58	460.36	± 0.10
Methylidyne (doublet), ² CH	C–H (to ^{eq} C)	334.65	338.77	± 0.10
	C–H (to ³ C)	334.65	338.77	± 0.10
	C–H (to ¹ C)	456.58	460.36	± 0.10
Methylidyne (quartet), ⁴ CH	C–H (to ^{eq} C)	262.89	267.00	± 0.59
	C–H (to ³ C)	262.89	267.00	± 0.59
	C–H (to ¹ C)	384.82	388.60	± 0.59

^aFor each reactant species, the dissociation that leads to standard products that are equilibrated over all electronic states, irrespective of their multiplicity, is listed first, immediately followed—if appropriate—by additional entries that correspond to dissociations of the same bond to nonstandard product species, which are assumed to be equilibrated only across the manifold of electronic states of a particular multiplicity, as indicated in parentheses (see text for further discussion on nonstandard species).

of the TN is earmarked for further development, typically by performing a new experimental or theoretical determination, such as that performed in the case of N atom.^{25,26}

For a typical gas-phase species that is newly inserted in the TN, the initial scaffolding of the pertinent TN section is established by entering the appropriate 0 K isogyric/isodesmic/homodesmic reaction enthalpies, BDEs, total atomization enthalpies, adiabatic ionization energies, or adiabatic electron affinities, based on a set of standard composite electronic structure computations carried out in-house using the Gaussian suite.²⁷ The set currently includes computations at the W1,^{28,29} G4,³⁰ CBS-APNO,^{31,32} G3X,³³ and CBS-QB3^{34,35} levels of theory and, for species inserted in the TN earlier on, may include results obtained at the G3,³⁶ G3B3,³⁷ and even CBS-Q³² levels of theory. This scaffold is subsequently fortified by adding relevant experimental and theoretical determinations from the literature. The constant expansion of the TN by adding high-quality measurements or computations, resulting in continuous improvements in the ensuing thermochemistry, is one of the important features of the ATcT approach. Except for species that suffer from a pronounced paucity of published thermochemical determinations of significance, the subsequent additions to the TN are normally of sufficiently high quality that the elements of the initial scaffold end up contributing negligibly to the final ATcT thermochemistry.

The ATcT BDEs and the corresponding ATcT enthalpies of formation that are presented here were obtained by analyzing and solving the current TN (ver. 1.122), which spans 1180 species and encompasses more than 19 000 determinations. The provenances of the ATcT enthalpies of formation of the targeted chemical species were analyzed by variance decomposition, allowing the identification of the most relevant contributors to the final thermochemistry of each species.

RESULTS AND DISCUSSION

The values of the 0 K bond dissociation energy, D_0 , and the 298.15 K bond dissociation enthalpy, BDE_{298} , are organized in three tables. The bond dissociations involving the methane–methyl–methylene–methylidyne–carbon atom sequence are listed in Table 1, all possible sequential dissociations starting from ethane are given in Table 2, and those starting from methanol are given in Table 3. In Table 1, the first entry for each reactant species corresponds to the dissociation of the corresponding C–H bond to standard products, which are equilibrated over all electronic states, irrespective of their multiplicity. In appropriate cases, this is followed by additional entries that correspond to the dissociation of the same reactant to nonstandard species, which are equilibrated only across the manifold of electronic states of a particular multiplicity. *Mutatis mutandis*, Tables 2 and 3 follow an analogous format, with the provision that in those tables most reactant species can have more than one type of bond dissociated (different C–H bonds in cases where not all hydrogen atoms are equivalent, C–C bond, and, in the methanol system, O–H bond and C–O bond). In these two tables, the first entry for a particular type of bond always corresponds to dissociation to standard products.

The corresponding standard enthalpies of formation for the related C₁ and C₂ hydrocarbon, oxohydrocarbon, or oxyhydrocarbon species, CH_n ($n = 1–4$), C₂H_n ($n = 1–6$), and COH_n ($n = 1–4$), are summarized in Table 4. For the sake of completeness, Table 4 also includes CO_n ($n = 1,2$), H_nO ($n = 1,2$), and the C, O, and H atoms.

For a handful of species discussed here, the currently achieved accuracies warrant the presentation of their thermochemistry to three digits beyond the decimal point.³⁸ In all other cases, the thermochemical values are presented here with two digits beyond the decimal point, the associated

Table 2. Sequential Bond Dissociation Enthalpies of Ethane (kJ/mol)

Species	Dissociating Bond ^a	0 K	298.15 K	Uncert.
Ethane, CH ₃ CH ₃	H–CH ₂ CH ₃	415.25	421.77	± 0.26
	CH ₃ –CH ₃	367.87	376.66	± 0.19
Ethyl, CH ₃ CH ₂	H–CH ₂ CH ₂	146.08	150.59	± 0.27
	CH ₃ CH–H (to ^{eq} CH ₃ CH)	446.57	452.61	± 0.82
	CH ₃ CH–H (to ³ CH ₃ CH)	446.57	452.59	± 0.82
	CH ₃ CH–H (to ¹ CH ₃ CH)	459.04	464.84	± 0.87
	CH ₃ –CH ₂ (to ^{eq} CH ₂)	409.83	418.03	± 0.31
	CH ₃ –CH ₂ (to ³ CH ₂)	409.83	418.03	± 0.31
	CH ₃ –CH ₂ (to ¹ CH ₂)	447.49	455.55	± 0.31
Ethylene, CH ₂ CH ₂	H–CHCH ₂	456.18	462.46	± 0.33
	CH ₂ –CH ₂ (to ^{eq} CH ₂)	720.96	730.59	± 0.24
	CH ₂ –CH ₂ (to ³ CH ₂ + ³ CH ₂)	720.96	730.59	± 0.24
	CH ₂ –CH ₂ (to ³ CH ₂ + ¹ CH ₂)	758.62	768.10	± 0.24
	CH ₂ –CH ₂ (to ¹ CH ₂ + ¹ CH ₂)	796.28	805.62	± 0.26
Ethylidene (equilib.), ^{eq} CH ₃ CH	H–CH ₂ CH	155.69	160.44	± 0.87
	CH ₃ C–H (to ^{eq} CH ₃ C)	363.1 ₆	368.4 ₁	± 1.1 ₈
	CH ₃ C–H (to ² CH ₃ C)	363.1 ₆	368.4 ₁	± 1.1 ₈
	CH ₃ C–H (to ⁴ CH ₃ C)	495.2 ₀	499.6 ₀	± 1.4 ₄
	CH ₃ –CH (to ^{eq} CH)	381.12	388.02	± 0.82
	CH ₃ –CH (to ² CH)	381.12	388.02	± 0.82
	CH ₃ –CH (to ⁴ CH)	452.8 ₈	459.7 ₈	± 1.0 ₀
Ethylidene (triplet), ³ CH ₃ CH	H–CH ₂ CH	155.69	160.46	± 0.87
	CH ₃ C–H (to ^{eq} CH ₃ C)	363.1 ₆	368.4 ₃	± 1.1 ₈
	CH ₃ C–H (to ² CH ₃ C)	363.1 ₆	368.4 ₃	± 1.1 ₈
	CH ₃ C–H (to ⁴ CH ₃ C)	495.2 ₀	499.6 ₂	± 1.4 ₄
	CH ₃ –CH (to ^{eq} CH)	381.12	388.04	± 0.82
	CH ₃ –CH (to ² CH)	381.12	388.04	± 0.82
	CH ₃ –CH (to ⁴ CH)	452.8 ₈	459.8 ₀	± 1.0 ₀
Ethylidene (singlet), ¹ CH ₃ CH	H–CH ₂ CH	143.21	148.21	± 0.91
	CH ₃ C–H (to ^{eq} CH ₃ C)	350.6 ₉	356.1 ₈	± 1.2 ₁
	CH ₃ C–H (to ² CH ₃ C)	350.6 ₉	356.1 ₈	± 1.2 ₁
	CH ₃ C–H (to ⁴ CH ₃ C)	482.7 ₃	487.3 ₇	± 1.4 ₆
	CH ₃ –CH (to ^{eq} CH)	368.64	375.79	± 0.87
	CH ₃ –CH (to ² CH)	368.64	375.79	± 0.87
	CH ₃ –CH (to ⁴ CH)	440.4 ₁	447.5 ₆	± 1.0 ₅
Vinyl, CH ₂ CH	H–CHCH	143.76	149.36	± 0.32
	CH ₂ C–H	326.21	333.29	± 0.40
	CH ₂ –CH (to ^{eq} CH ₂ + ^{eq} CH)	682.63	690.72	± 0.36
	CH ₂ –CH (to ³ CH ₂ + ² CH)	682.63	690.72	± 0.36
	CH ₂ –CH (to ³ CH ₂ + ⁴ CH)	754.40	762.49	± 0.68
	CH ₂ –CH (to ¹ CH ₂ + ² CH)	720.29	728.24	± 0.36
	CH ₂ –CH (to ¹ CH ₂ + ⁴ CH)	792.06	800.00	± 0.68
Ethylidyne (equilib.), ^{eq} CH ₃ C	H–CH ₂ C	118.74	125.31	± 0.92
	CH ₃ –C (to ^{eq} C)	352.61	358.38	± 0.87
	CH ₃ –C (to ³ C)	352.61	358.38	± 0.87
	CH ₃ –C (to ¹ C)	474.54	479.97	± 0.87
Ethylidyne (doublet), ² CH ₃ C	H–CH ₂ C	118.74	125.31	± 0.92
	CH ₃ –C (to ^{eq} C)	352.61	358.38	± 0.87
	CH ₃ –C (to ³ C)	352.61	358.38	± 0.87
	CH ₃ –C (to ¹ C)	474.54	479.97	± 0.87
Ethylidyne (quartet), ⁴ CH ₃ C	H–CH ₂ C	-13.3 ₀	-5.8 ₇	± 1.2 ₄
	CH ₃ –C (to ^{eq} C)	220.5 ₇	227.1 ₉	± 1.2 ₁
	CH ₃ –C (to ³ C)	220.5 ₇	227.1 ₉	± 1.2 ₁
	CH ₃ –C (to ¹ C)	342.5 ₀	348.7 ₈	± 1.2 ₁
Acetylene, HCCH	H–CCH	551.072	557.709	± 0.078
	HC–CH (to ^{eq} CH + ^{eq} CH)	956.73	963.96	± 0.21
	HC–CH (to ² CH + ² CH)	956.73	963.96	± 0.21
	HC–CH (to ² CH + ⁴ CH)	1028.5 ₀	1035.7 ₂	± 0.62
	HC–CH (to ⁴ CH + ⁴ CH)	1100.2 ₆	1107.4 ₈	± 1.1 ₈

Table 2. continued

Species	Dissociating Bond ^a	0 K	298.15 K	Uncert.
Vinylidene, CH ₂ C	H–CHC	368.62	373.78	± 0.32
	CH ₂ –C (to ^{eq} CH ₂ + ^{eq} C)	691.08	696.20	± 0.33
	CH ₂ –C (to ³ CH ₂ + ³ C)	691.08	696.20	± 0.33
	CH ₂ –C (to ³ CH ₂ + ¹ C)	813.01	817.80	± 0.33
	CH ₂ –C (to ¹ CH ₂ + ³ C)	728.74	733.72	± 0.33
	CH ₂ –C (to ¹ CH ₂ + ¹ C)	850.67	855.31	± 0.33
Ethynyl, HCC	H–CC (to ^{eq} C ₂)	472.37	478.69	± 0.26
	H–CC (to ¹ C ₂)	472.37	476.79	± 0.26
	H–CC (to ³ C ₂)	479.54	484.10	± 0.26
	HC–C (to ^{eq} CH + ^{eq} C)	740.31	745.02	± 0.15
	HC–C (to ² CH + ³ C)	740.31	745.02	± 0.15
	HC–C (to ² CH + ¹ C)	862.24	866.61	± 0.15
	HC–C (to ⁴ CH + ³ C)	812.08	816.78	± 0.60
	HC–C (to ⁴ CH + ¹ C)	934.01	938.37	± 0.60
Ethynylene (equilib.), ^{eq} C ₂	C–C (to ^{eq} C + ^{eq} C)	602.59	605.10	± 0.25
	C–C (to ³ C + ³ C)	602.59	605.10	± 0.25
	C–C (to ³ C + ¹ C)	724.52	726.69	± 0.25
	C–C (to ¹ C + ¹ C)	846.45	848.28	± 0.25
Ethynylene (singlet), ¹ C ₂	C–C (to ^{eq} C + ^{eq} C)	602.59	606.99	± 0.25
	C–C (to ³ C + ³ C)	602.59	606.99	± 0.25
	C–C (to ³ C + ¹ C)	724.52	728.58	± 0.25
	C–C (to ¹ C + ¹ C)	846.45	850.17	± 0.25
Ethynylene (triplet), ³ C ₂	C–C (to ^{eq} C + ^{eq} C)	595.42	599.69	± 0.25
	C–C (to ³ C + ³ C)	595.42	599.69	± 0.25
	C–C (to ³ C + ¹ C)	717.35	721.28	± 0.25
	C–C (to ¹ C + ¹ C)	839.28	842.87	± 0.25

^aWith the exception of C₂, more than one type of bond is listed for each reactant species; for each type of bond, the dissociation leading to standard products that are equilibrated over all electronic states, irrespective of their multiplicity, is listed first, immediately followed—if appropriate—by additional entries that correspond to dissociations of the same bond to nonstandard product species, which are assumed to be equilibrated only across the manifold of electronic states of a particular multiplicity, as indicated in parentheses (see text for further discussion on nonstandard species).

uncertainties then having two significant digits in all but several cases where they are slightly larger than ±1 kJ/mol. The systematic presentation of results with two digits beyond the decimal point is retained even there, but the second digit is subscripted to indicate its diminished significance.

ATcT Value for $\Delta_fH^\circ(H)$. The enthalpy of formation of hydrogen atom is one of the most fundamental thermochemical quantities. Since its knowledge relates to the definition of all the C–H and O–H BDEs discussed below, it is quoted at the beginning of this discussion. The current ATcT value is the same as that given previously:^{14,17–19} $\Delta_fH^\circ_{298}(H) = 217.998 \pm 0.001$ kJ/mol (216.034 kJ/mol at 0 K), truncated here to three digits, and apart from further improvement in accuracy, it coincides with the CODATA value²² (217.998 ± 0.006 kJ/mol at 298.15 K). The genesis of the ATcT value has been discussed earlier^{14,19} and will not be repeated here.

ATcT Value for $\Delta_fH^\circ(CH_4)$. The current ATcT enthalpy of formation of methane, $\Delta_fH^\circ_{298}(CH_4) = -74.520 \pm 0.056$ kJ/mol (−66.550 kJ/mol at 0 K), is slightly more accurate than, but otherwise nearly identical to the value published in the first set of ATcT results¹⁴ (−74.549 ± 0.060 kJ/mol at 298.15 K), which were obtained from the original—significantly smaller—TN. The ATcT value is between 5 and 7 times more accurate than the widely used values from Pedley et al.³⁹ (−74.4 ± 0.4 kJ/mol at 298.15 K), Gurvich et al.²⁴ (−74.60 ± 0.30 kJ/mol at 298.15 K), JANAF tables²³ (−74.87 ± 0.34 kJ/mol at 298.15 K), or NBS tables^{40,41} (−74.81 ± 0.40 kJ/mol at 298.15 K).

The values for $\Delta_fH^\circ(CH_4)$ found in traditional compilations are based either on the combustion calorimetric determination by Pittam and Pilcher⁴² (Pedley et al.) or on the similar but older measurement of Rossini^{43–45} (JANAF, and—apparently—NBS), or taken as an average of the two (Gurvich et al.). The ATcT TN includes both calorimetric measurements, as well as a similar determination by Roth and Banse⁴⁶ and more recent calorimetry by Dale et al.⁴⁷ and by Alexandrov et al.^{48,49} It also includes our second and third law reanalysis¹⁴ of the high-temperature hydrogen/methane/graphite equilibrium study of Smith.⁵⁰ Variance decomposition analysis indicates that the provenance of the ATcT value for $\Delta_fH^\circ(CH_4)$ involves a much larger number of contributors than the traditionally derived values discussed above: In order to pedigree 90% of the provenance, it takes as many as 59 different determinations, and explaining 99% of the provenance involves no less than 1217 determinations (and 4570 determinations to pedigree 99.9% of the provenance, etc.). Further analysis shows that the largest single contributor (67.1%) is the third law Gibbs energy extracted from the equilibrium study of Smith.⁵⁰ The next most important contributions come from the five calorimetric studies mentioned above (10.8% as a group, ranging individually from 4.1% for the study of Dale et al. to 1.0% for the study of Pittam and Pilcher). Notably, the ATcT provenance also features as one of the top contributions the calorimetric study of combustion of hydrogen to form liquid water by Rossini^{45,51,52} (at 2.2%). The contributions of theoretical determinations are relatively modest for CH₄; the top theoretical contributors are

Table 3. Sequential Bond Dissociation Enthalpies of Methanol, Carbon Dioxide, and Water (kJ/mol)

Species ^a	Dissociating Bond ^b	0 K	298.15 K	Uncert.
Methanol, CH ₃ OH	H–CH ₂ OH	395.60	402.14	± 0.32
	CH ₃ O–H	434.76	440.24	± 0.34
	CH ₃ –OH	376.86	384.57	± 0.18
Hydroxymethyl, CH ₂ OH	H–CHOH (to ^{eq} HCOH)	338.69	343.21	± 0.45
	H–CHOH (to ^{t-1} HCOH)	338.69	343.20	± 0.45
	H–CHOH (to ^{c-1} HCOH)	357.15	361.68	± 0.46
	H–CHOH (to ³ HCOH)	445.3 ₀	450.6 ₃	± 1.1 ₅
	CH ₂ O–H	120.94	125.38	± 0.33
	CH ₂ –OH (to ^{eq} CH ₂)	438.47	445.58	± 0.34
	CH ₂ –OH (to ³ CH ₂)	438.47	445.58	± 0.34
	CH ₂ –OH (to ¹ CH ₂)	476.13	483.09	± 0.35
Methoxy, CH ₃ O	H–CH ₂ O	81.78	87.28	± 0.35
	CH ₃ –O (to ^{eq} O)	367.73	374.07	± 0.35
	CH ₃ –O (to ³ O)	367.73	374.07	± 0.35
	CH ₃ –O (to ¹ O)	557.55	563.37	± 0.35
Formaldehyde, CH ₂ O	H–CHO	362.810	368.988	± 0.006
	CH ₂ –O (to ^{eq} CH ₂ + ^{eq} O)	743.15	749.93	± 0.15
	CH ₂ –O (to ³ CH ₂ + ³ O)	743.15	749.93	± 0.15
	CH ₂ –O (to ³ CH ₂ + ¹ O)	932.97	939.23	± 0.15
	CH ₂ –O (to ¹ CH ₂ + ³ O)	780.81	787.45	± 0.16
	CH ₂ –O (to ¹ CH ₂ + ¹ O)	970.64	976.74	± 0.16
Hydroxymethylene (equilb.), ^{eq} HCOH	H–COH	320.94	327.04	± 0.73
	HCO–H	145.06	151.16	± 0.32
	HC–OH (to ^{eq} CH)	517.63	524.97	± 0.34
	HC–OH (to ² CH)	517.63	524.97	± 0.34
	HC–OH (to ⁴ CH)	589.40	596.73	± 0.67
Hydroxymethylene (trans), ^{t-1} HCOH	H–COH	320.94	327.06	± 0.73
	HCO–H	145.06	151.17	± 0.32
	HC–OH (to ^{eq} CH)	517.63	524.98	± 0.34
	HC–OH (to ² CH)	517.63	524.98	± 0.34
	HC–OH (to ⁴ CH)	589.40	596.74	± 0.67
Hydroxymethylene (cis), ^{c-1} HCOH	H–COH	302.48	308.57	± 0.74
	HCO–H	126.60	132.69	± 0.33
	HC–OH (to ^{eq} CH)	499.17	506.50	± 0.35
	HC–OH (to ² CH)	499.17	506.50	± 0.35
	HC–OH (to ⁴ CH)	570.94	578.26	± 0.68
Hydroxymethylene (triplet), ³ HCOH	H–COH	214.3 ₃	219.6 ₃	± 1.2 ₈
	HCO–H	38.4 ₅	43.7 ₄	± 1.1 ₀
	HC–OH (to ^{eq} CH)	411.0 ₂	417.5 ₅	± 1.1 ₁
	HC–OH (to ² CH)	411.0 ₂	417.5 ₅	± 1.1 ₁
	HC–OH (to ⁴ CH)	482.7 ₉	489.3 ₁	± 1.2 ₅
Formyl, HCO	H–CO	60.81	65.67	± 0.10
	HC–O (to ^{eq} CH + ^{eq} O)	798.20	803.54	± 0.14
	HC–O (to ² CH + ³ O)	798.20	803.54	± 0.14
	HC–O (to ² CH + ¹ O)	988.02	992.84	± 0.14
	HC–O (to ⁴ CH + ³ O)	869.97	875.31	± 0.60
	HC–O (to ⁴ CH + ¹ O)	1059.79	1064.60	± 0.60
Isoformyl, COH	CO–H	-115.07	-110.21	± 0.67
	C–OH (to ^{eq} C)	531.35	536.69	± 0.67
	C–OH (to ³ C)	531.35	536.69	± 0.67
	C–OH (to ¹ C)	653.28	658.28	± 0.67
Carbon dioxide, CO ₂	O–CO (to ^{eq} O)	526.150	532.181	± 0.025
	O–CO (to ³ O)	526.150	532.181	± 0.025
	O–CO (to ¹ O)	715.971	721.475	± 0.025

Table 3. continued

Species ^a	Dissociating Bond ^b	0 K	298.15 K	Uncert.
Carbon monoxide, CO	C–O (to ^{eq} C + ^{eq} O)	1072.047	1076.638	± 0.051
	C–O (to ³ C + ³ O)	1072.047	1076.638	± 0.051
	C–O (to ³ C + ¹ O)	1261.869	1265.931	± 0.051
	C–O (to ¹ C + ³ O)	1193.978	1198.230	± 0.051
	C–O (to ¹ C + ¹ O)	1383.800	1387.524	± 0.051
Water, H ₂ O	H–OH	492.215	497.321	± 0.002
Hydroxyl, OH	O–H (to ^{eq} O)	425.628	429.737	± 0.027
	O–H (to ³ O)	425.628	429.737	± 0.027
	O–H (to ¹ O)	615.450	619.031	± 0.027

^aFor the sake of completeness, BDEs of CO₂ and H₂O are also presented here. ^bNearly every dissociating species in the table has more than one type of bond listed; for each type of bond, the dissociation leading to standard products that are equilibrated over all electronic states, irrespective of their multiplicity, is listed first, immediately followed—if appropriate—by additional entries that correspond to dissociations of the same bond to nonstandard product species, which are assumed to be equilibrated only across the manifold of electronic states of a particular multiplicity, as indicated in parentheses (see text for further discussion on nonstandard species).

the 0 K total atomization energies TAE₀(CH₄) obtained by Karton et al.⁵³ at the W4.4 level of theory (0.5%) and by Harding et al.⁵⁴ at the HEAT 345-QP level of theory (0.4%). The remainder of the provenance (amounting to 18.9%) is thinly dispersed through a large number of contributions of 0.5% or less each.

Determinations that do not include the target species as either reagent or product, such as the combustion calorimetry of hydrogen mentioned above, may *prima facie* appear as surprising interlopers, until it is realized that such determinations are needed to close various thermochemical cycles that potentially carry information on the enthalpy of formation of the target species. Since ATcT implicitly exploits every possible thermochemical cycle present in the TN, irrespective of its complexity, occurrences like these are quite normal when analyzing ATcT provenances.

Clearly, a calorimetric determination of the heat of combustion of methane, which produces carbon dioxide and liquid water, while obviously very important in the case of CH₄, cannot *per se* deliver Δ_fH°(CH₄) unless it is combined with some suitable way of defining the enthalpies of formation of the two products. In sequential thermochemistry, the necessary Δ_fH°(H₂O) and Δ_fH°(CO₂) are obtained (and then fixed) in two separate steps, both of which must precede the step that is targeting Δ_fH°(CH₄). Enthalpies of formation that are fixed in earlier steps and utilized in subsequent steps form a hidden web of progenitor–progeny dependences plaguing traditional thermochemical tables, effectively preventing their update with new data without introducing new inconsistencies. Contrary to traditional thermochemistry, such contributions are explicit in ATcT provenances.

ATcT Values for Δ_fH°(CH₃) and BDE(H–CH₃). The current ATcT enthalpy of formation of methyl, Δ_fH°₂₉₈(CH₃) = 146.374 ± 0.080 kJ/mol (149.788 kJ/mol at 0 K), is a noticeable improvement over the less accurate but otherwise compatible value obtained by a pre-ATcT attempt to manually set up, analyze, adjust, and solve a very small (localized) TN⁵⁵ (146.65 ± 0.30 kJ/mol at 298.15 K, which subsequently became the value recommended in the IUPAC-sponsored evaluation⁵⁶). The older 298.15 K values found in Tsang⁵⁷ (147 ± 1 kJ/mol), Berkowitz et al.⁵⁸ (146.4 ± 0.4 kJ/mol), JANAF²³ (145.69 ± 0.80 kJ/mol), Gurvich et al.²⁴ (146.30 ± 0.50 kJ/mol), and NBS^{40,41} (145.69 ± 0.40 kJ/mol) are also compatible but even less accurate.

Variance decomposition shows that the top 90% of the provenance of the ATcT enthalpy of formation of methyl involves 99 determinations, broadening to 1495 contributors to capture 99% of the provenance. The top contributor is the same as that found in the case of methane (third law Gibbs energy from the hydrogen/graphite/methane equilibrium study⁵⁰), albeit with a smaller relative contribution (23.7%). The reason for this is that the ATcT thermochemistry of CH₃ is correlated to that of CH₄ (with a correlation coefficient⁵⁹ of 0.595), and thus it is not surprising that the next seven contributors (totaling as a group 36.6%) are components of the positive ion cycle⁶⁰ that establishes the BDE of CH₄: the 0 K photoionization appearance energies (AE₀) of CH₃⁺ from CH₄ as determined by Bödi et al.⁶¹ using a jet source (16.2%) or an effusive beam source (1.8%), and similar AE₀ measurements by Weitzel et al.^{62,63} (8.4%), Litorja and Ruscic⁶⁴ (1.8%), and McCulloh and Dibeler⁶⁵ (1.8%), together with the adiabatic ionization energies (IE_a) of methyl as determined by Schulenburg et al.⁶⁶ (5.0%) and by Blush et al.⁶⁷ (1.6%). As in the case of CH₄, theory lags behind experiment in contributing to the provenance of Δ_fH°(CH₃). The top two theoretical contributions are the TAE₀ values for methyl at the HEAT 345-(Q) level of theory by Harding et al.⁵⁴ (1.5%) and at the W4.4 level of theory by Karton et al.⁶⁸ (1.2%).

The ATcT bond dissociation enthalpy of methane is BDE₂₉₈(H–CH₃) = 438.892 ± 0.065 kJ/mol (432.373 kJ/mol at 0 K), see Table 1. The quoted uncertainty for this BDE (as well as for all other ATcT BDEs discussed later and listed in the corresponding tables) has been obtained from ATcT by using the full covariance matrix. Notably, since Δ_fH°(CH₄) and Δ_fH°(CH₃) are moderately correlated, the correctly calculated uncertainty (±0.065 kJ/mol) is smaller than the corresponding uncertainty (±0.097 kJ/mol) that would be obtained by propagating the uncertainties of Δ_fH°(CH₄), Δ_fH°(CH₃), and Δ_fH°(H) in quadrature, since the latter scheme implicitly assumes that all covariances are zero. Although this is a recurring theme for a fair number of BDEs listed in Tables 1–3, it will not be separately discussed for other such cases.

As expected, the underlying provenance of BDE(H–CH₃) is also distributed (46 determinations to describe 90% of the provenance, 968 for 99%). Of note here is that the leading contributor to the individual provenances of Δ_fH°(CH₄) and Δ_fH°(CH₃) is not among the prominent contributors to the provenance of BDE(H–CH₃). The reason is that this determination is relevant in establishing the enthalpies of

Table 4. ATcT Standard Enthalpies of Formation, $\Delta_f H^\circ$ (kJ/mol), of CH_n , C_2H_n , COH_n , CO_n , and OH_n Species

Species ^a	0 K	298.15 K	Uncert.
Methane, CH_4	-66.550	-74.520	± 0.056
Methyl, CH_3	149.788	146.374	± 0.080
Methylene (equilib.), ${}^{\text{eq}}\text{CH}_2$	390.96	391.52	± 0.12
Methylene (triplet), ${}^3\text{CH}_2$	390.96	391.52	± 0.12
Methylene (singlet), ${}^1\text{CH}_2$	428.62	429.03	± 0.13
Methyldyne (equilib.), ${}^{\text{eq}}\text{CH}$	592.78	596.12	± 0.10
Methyldyne (doublet), ${}^2\text{CH}$	592.78	596.12	± 0.10
Methyldyne (quartet), ${}^4\text{CH}$	664.55	667.88	± 0.59
Carbon atom (equilib.), ${}^{\text{eq}}\text{C}$	711.401	716.886	± 0.050
Carbon atom (triplet), ${}^3\text{C}$	711.401	716.886	± 0.050
Carbon atom (singlet), ${}^1\text{C}$	833.332	838.478	± 0.050
Ethane, CH_3CH_3	-68.29	-83.91	± 0.14
Ethyl, CH_2CH_2	130.92	119.86	± 0.28
Ethylene, CH_2CH_2	60.96	52.45	± 0.13
Ethyldene (equilib.), ${}^{\text{eq}}\text{CH}_3\text{CH}$	361.45	354.47	± 0.82
Ethyldene (triplet), ${}^3\text{CH}_3\text{CH}$	361.45	354.45	± 0.82
Ethyldene (singlet), ${}^1\text{CH}_3\text{CH}$	373.93	366.70	± 0.86
Vinyl, CH_2CH	301.11	296.91	± 0.33
Ethyldyne (equilib.), ${}^{\text{eq}}\text{CH}_3\text{C}$	508.58	504.88	± 0.87
Ethyldyne (doublet), ${}^2\text{CH}_3\text{C}$	508.58	504.88	± 0.87
Ethyldyne (quartet), ${}^4\text{CH}_3\text{C}$	640.6 ₂	636.0 ₇	$\pm 1.2_0$
Acetylene, HCCH	228.84	228.27	± 0.13
Vinylidene, CH_2C	411.29	412.20	± 0.33
Ethynyl, HCC	563.87	567.99	± 0.15
Ethynylene (equilib.), ${}^{\text{eq}}\text{C}_2$	820.21	828.68	± 0.27
Ethynylene (singlet), ${}^1\text{C}_2$	820.21	826.78	± 0.27
Ethynylene (triplet), ${}^3\text{C}_2$	827.38	834.08	± 0.27
Methanol, CH_3OH	-189.83	-200.71	± 0.16
Hydroxymethyl, CH_2OH	-10.26	-16.57	± 0.33
Methoxy, CH_3O	28.90	21.53	± 0.34
Formaldehyde, CH_2O	-105.35	-109.19	± 0.10
Hydroxymethylene (equilib.), ${}^{\text{eq}}\text{HCOH}$	112.40	108.64	± 0.33
Hydroxymethylene (trans), $t^{-1}\text{HCOH}$	112.40	108.63	± 0.33
Hydroxymethylene (cis), $c^{-1}\text{HCOH}$	130.86	127.11	± 0.34
Hydroxymethylene (triplet), ${}^3\text{HCOH}$	219.0 ₁	216.0 ₆	$\pm 1.1_0$
Formyl, HCO	41.43	41.80	± 0.10
Isoformyl, COH	217.31	217.69	± 0.67
Carbon dioxide, CO_2	-393.109	-393.475	± 0.014
Carbon monoxide, CO	-113.803	-110.523	± 0.026
Water, H_2O	-238.930	-241.834	± 0.026
Hydroxyl, OH	37.250	37.490	± 0.026
Oxygen atom (equilib.), ${}^{\text{eq}}\text{O}$	246.844	249.229	± 0.002
Oxygen atom (triplet), ${}^3\text{O}$	246.844	249.229	± 0.002
Oxygen atom (singlet), ${}^1\text{O}$	436.666	438.523	± 0.002
Hydrogen atom, H	216.034	217.998	± 0.001

^aThe table contains both standard and nonstandard species. Species without any additional annotations, and those marked as equilibrated, are standard (regular) species, assumed to thermally equilibrate at $T > 0$ across all electronic states, irrespective of their spin multiplicity. Species with additional annotations are nonstandard, in the sense that they are assumed to thermally equilibrate only across the manifold of electronic states of a particular multiplicity (see text for additional discussion).

formation of CH_3 and CH_4 on an absolute scale, but its influence largely cancels out when the BDE is computed. Thus, the top seven contributors to $\text{BDE}(\text{H}-\text{CH}_3)$ are the positive ion cycle components already discussed for $\Delta_f H^\circ(\text{CH}_3)$: the AE_0 determinations by Bödi et al.⁶¹ (31.0% and 3.4%), Weitzel et al.^{62,63} (16.2%), Litorja and Ruscic⁶⁴ (3.4%), McCulloh and Dibeler⁶⁵ (3.4%), and the IE_a of Schulenburg et al.⁶⁶ (9.5%) and Blush et al.⁶⁷ (3.1%).

ATcT Values for $\Delta_f H^\circ(\text{CH}_2)$, Singlet–Triplet Gap in Methylenes, and $\text{BDE}(\text{H}-\text{CH}_2)$. Methylenes are represented in ATcT as three thermodynamically distinct species: regular methylene (denoted here simply by CH_2 , or using the notation ${}^{\text{eq}}\text{CH}_2$ when emphasis is necessary, such as in Tables 1–4), triplet-only methylene (shorthand notation ${}^3\text{CH}_2$), and singlet-

only methylene (shorthand notation ${}^1\text{CH}_2$). Regular methylene, CH_2 , corresponds to the methylene species found in standard compilations, such as the NBS tables,^{40,41} JANAF tables,²³ or Gurvich et al.,²⁴ and at $T > 0$ it is assumed to be thermally equilibrated over all available electronic states (triplet and singlet). As the name suggests, the singlet-only methylene species, ${}^1\text{CH}_2$, is assumed to be equilibrated only within the manifold of singlet states, and, by analogy, the triplet-only methylene species, ${}^3\text{CH}_2$, is assumed to be equilibrated only within the manifold of triplet states. Since the ground state of methylene is ${}^3\text{B}_1$, $\Delta_f H^\circ({}^{\text{eq}}\text{CH}_2) \equiv \Delta_f H^\circ({}^3\text{CH}_2)$, although at other temperatures these two enthalpies are not identical. However, the $X^3\text{B}_1 - a^1\text{A}_1$ gap in methylene is large enough so that the contribution of the singlet states to the enthalpy increment of regular methylene is quite small at 298.15 K (<0.001 kJ/mol with the present ATcT partition functions for methylene, which include anharmonic corrections but will not be otherwise discussed here), and thus $\Delta_f H^\circ_{298}({}^{\text{eq}}\text{CH}_2) \approx \Delta_f H^\circ_{298}({}^3\text{CH}_2)$, at least within the limit of the present uncertainties. At sufficiently high temperatures, such as those encountered in combustion, $\Delta_f H^\circ_T({}^{\text{eq}}\text{CH}_2) \neq \Delta_f H^\circ_T({}^3\text{CH}_2)$. It is probably useful to point out here that one could regard triplet-only and singlet-only methylene as partial thermochemical species and that the thermochemical properties of methylene as a whole can be at any time obtained from a weighted sum of the thermochemical properties of the two nonstandard species, where the weights represent their relative concentrations. In particular, the thermochemical properties of regular methylene exactly correspond to the properties of a thermally equilibrated mixture of triplet-only and singlet-only methylene species. The ability to thermochemically distinguish regular, triplet-only, and singlet-only methylene and carry separate bookkeeping for triplet-only and singlet-only methylene in chemical models may be relevant in situations when a reaction (or a scavenger species) consumes preferentially one of the two multiplicities, but not the other.^{69,70} Furthermore, thermal equilibration across different multiplicities is not necessarily as efficient as the thermal equilibration within the manifold of electronic states of the same multiplicity. This kind of phenomenon has been inferred to occur in photoionization experiments involving the analogous silylene,⁷¹ SiH_2 . Noting that the ordering of the lowest singlet and triplet state in silylene is the reverse of that found in methylene, in those experiments the excited triplet silylene was clearly observed to resist collisional relaxation to the ground singlet state in an *in situ* source of radicals that successfully provided efficient thermal equilibration in other cases.^{58,72}

The current ATcT enthalpies of formation for methylene are $\Delta_f H^\circ_{298}({}^{\text{eq}}\text{CH}_2) = \Delta_f H^\circ_{298}({}^3\text{CH}_2) = 391.52 \pm 0.12$ kJ/mol (390.96 kJ/mol at 0 K) and $\Delta_f H^\circ_{298}({}^1\text{CH}_2) = 429.03 \pm 0.13$ kJ/mol (428.62 kJ/mol at 0 K). These can be compared to the values recommended by the IUPAC-sponsored evaluation⁵⁶ (391.2 ± 1.6 kJ/mol for regular and triplet-only and 428.8 ± 1.6 kJ/mol for singlet-only, both at 298.15 K) and to the older 298.15 K values for regular methylene found in NBS tables^{40,41} (390.37 ± 0.40 kJ/mol), JANAF tables²³ (386.4 ± 4.2 kJ/mol), and Gurvich et al.²⁴ (390.4 ± 4.0 kJ/mol).

Variance decomposition shows that 90% of the provenance of the ATcT values for methylene is accounted for by 263 determinations (regular and triplet-only methylene) or 262 determinations (singlet-only), increasing to 1948 (regular), 691 (triplet-only), and 1881 (singlet-only) to account for 99% of the provenance. As opposed to the cases of methane and

methyl, theoretical determinations rank noticeably higher for the three methylene species, and the individual weights of prominent contributors are dispersed much more evenly. For regular methylene, there are 12 determinations with individual contributions of 2% or more, 10 of which come from theory and two from experiment. The theoretical contributions include values obtained by the Feller–Peterson–Dixon (FPD) approach⁷³ for TAE₀ of triplet and singlet methylene, as well as D₀(H–CH) together with D₀(CH) (6.1, 3.0, 2.0, and 2.3%, respectively), D₀(H–CH) and TAE₀ for triplet methylene obtained by the focal point (FP) approach⁷⁴ (4.3 and 2.5%), TAE₀ for triplet methylene and D₀(H–CH₂) obtained from the HEAT 345-QP approach⁵⁴ (3.0% each) and from the W4.4 approach⁶⁸ (2.4% each). The top two experimental contributions are the photoionization AE₀ of CH₂⁺ from CH₃ measured by Litorja and Ruscic⁶⁴ (2.8%) and the previously discussed hydrogen/graphite/methane equilibrium constant⁵⁰ (2.1%). The lineups of contributors to the provenances of Δ_fH°(³CH₂) and Δ_fH°(¹CH₂) are quite similar to those for regular methylene (though with slightly different percentages), with the addition of the singlet–triplet separation obtained by Jensen and Bunker⁷⁵ as the top contributor (8.0%) in the case of singlet-only methylene.

It is worthwhile, at this point, to make an additional comment on the ATcT value for Δ_fH°(CH₂). Namely, in the current TN, four out of the 12 top contributors to the enthalpies of formation of methylene come from the same theoretical paper,⁷³ and one might thus start worrying whether the resulting ATcT value is somewhat biased by one particular set of theoretical results. The answer can be obtained rather straightforwardly by comparison to the ATcT value that is based on the last version of the TN prior to inclusion of the FPD results. This quantity was recently published¹⁹ as an interim ATcT value (391.52 ± 0.13 kJ/mol for regular and 429.04 ± 0.14 kJ/mol for singlet-only methylene, both at 298.15 K) and was, in fact, used to independently benchmark⁷³ the FPD results. Clearly, the comparison shows that adding the FPD calculations to the TN further improved the accuracy of the resulting ATcT enthalpy of formation of methylene and enhanced its robustness (by broadening its provenance), while the actual value stayed the same for all practical purposes, except for a barely perceptible change in the least significant digit. In fact, this is an excellent illustration of the mutually beneficial interplay between state-of-the-art electronic structure methods and ATcT, which often exhibits a two-way flow of information: Independently obtained ATcT results are initially used in the development and/or benchmarking of a theoretical method,^{54,73,76–78} but once the method has been evaluated and its expected accuracy is established, the new computational results are ready to be incorporated in the next version of the TN, leading to additional improvements of the resulting ATcT thermochemistry.

The ATcT value for the triplet–singlet gap in methylene is 37.662 ± 0.052 kJ/mol (3148.3 ± 4.3 cm⁻¹) at 0 K, corresponding to an enthalpy difference between triplet-only and singlet-only methylene of 37.517 kJ/mol at 298.15 K. The ATcT value is in excellent agreement with the prior most accurate value, 3147 ± 5 cm⁻¹, obtained by Jensen and Bunker,⁷⁵ and the accurate theoretical values of 3138 ± 34 cm⁻¹ (Császár et al.⁷⁴), 37.8 ± 1 kJ/mol (Karton et al.⁷⁹), and 37.66 ± 2 kJ/mol (Aguilera-Iparraguirre et al.⁷⁷), as well as with the experimental value of 37.7 ± 0.4 kJ/mol (Leopold et al.⁸⁰),

and is also in very good agreement with a rather large number of earlier experimental and theoretical determinations.

The bond dissociation enthalpy of methyl, BDE₂₉₈(H–CH₂), is 463.14 ± 0.13 kJ/mol (457.21 kJ/mol at 0 K) to form either regular methylene or nonstandard triplet-only methylene, and 500.66 ± 0.13 kJ/mol (494.87 kJ/mol at 0 K) to form singlet-only methylene (see Table 1).

ATcT Values for Δ_fH°(CH) and BDE(H–CH). In complete analogy to methylene, in ATcT, methylidyne is also represented as three thermochemically distinct species: regular methylidyne (⁰CH, or simply CH), doublet-only methylidyne (²CH), and quartet-only methylidyne (⁴CH). By definition, Δ_fH°₀(CH) ≡ Δ_fH°₀(²CH). In addition—as was the case for methylene—the difference between the enthalpy of formation of regular and doublet-only methylidyne is sufficiently small at 298.15 K, so that Δ_fH°₂₉₈(CH) ≡ Δ_fH°₂₉₈(²CH).

The ATcT enthalpies of formation are Δ_fH°₂₉₈(CH) = Δ_fH°₂₉₈(²CH) = 596.12 ± 0.10 kJ/mol (592.78 kJ/mol at 0 K), and Δ_fH°₂₉₈(⁴CH) = 667.88 ± 0.59 kJ/mol (664.55 kJ/mol at 0 K). The current ATcT value for regular methylidyne is essentially identical to the previous interim ATcT value¹⁹ (596.16 ± 0.12 kJ/mol at 298.15 K) and is significantly more accurate than the corresponding quantities found in NBS tables^{40,41} (595.80 ± 0.40 kJ/mol), JANAF tables²³ (594.1 ± 17.5 kJ/mol), Gurvich et al.²⁴ (597.4 ± 1.3 kJ/mol), and the more recent IUPAC-sponsored evaluation⁵⁶ (595.8 ± 0.6 kJ/mol).

Variance decomposition indicates that 279 determinations are responsible for 90% of the provenance of the ATcT enthalpy of formation of regular methylidyne (2188 determinations for 99%). There are five determinations that contribute at 2% or more each, all of which are from theory: D₀(CH) obtained by the FPD approach⁷³ (23.0%), FP approach⁸¹ (5.6%), and HEAT 345-QP approach⁵⁴ (2.1%), an earlier version of D₀(CH) from the FPD approach⁸² (3.7%), and D₀(³CH₂) from the FP approach⁷⁴ (2.4%). The experimental determinations rank rather low on the list of contributors, because they lag significantly in accuracy. The provenance in the case of ²CH appears rather similar, while in the case of ⁴CH the top contributor (55.0%) is the experimental determination of the doublet–quartet gap that Kasdan et al.⁸³ obtained by photoelectron spectroscopy of CH⁻.

The ATcT value for the bond dissociation enthalpy of either regular or triplet-only methylene to produce either regular or doublet-only methylidyne is BDE₂₉₈(H–CH) = 422.60 ± 0.12 kJ/mol (417.86 kJ/mol at 0 K), and to produce quartet-only methylidyne is BDE₂₉₈(H–CH) = 494.36 ± 0.60 kJ/mol (489.62 kJ/mol at 0 K). The bond dissociation enthalpy of singlet-only methylene to produce regular or doublet-only methylidyne is BDE₂₉₈(H–CH) = 385.08 ± 0.13 kJ/mol (380.20 kJ/mol at 0 K), and to produce quartet-only methylidyne is BDE₂₉₈(H–CH) = 456.84 ± 0.60 kJ/mol (451.96 kJ/mol at 0 K).

ATcT Values for Δ_fH°(C) and BDE(CH). In order to define BDE(CH), beside Δ_fH°(CH) one also needs the enthalpy of formation of C atom. In analogy to methylene and methylidyne, in ATcT C atom is represented as three species: regular (⁰C or C), triplet-only (³C), and singlet-only (¹C).

A detailed discussion of the (rather complex) genesis of the ATcT value for C atom is outside the scope of this paper. Suffice it to mention here that, in the earliest stages of development of ATcT, as the first ATcT TN was constructed and analyzed, it became evident relatively quickly that the

measurement of $D_0(\text{CO})$ by Douglas and Møller,⁸⁴ which was used by the CODATA critical evaluation²² to obtain $\Delta_f H^\circ(\text{C})$, is likely to lead to a somewhat underestimated enthalpy of formation for the C atom. Namely, Douglas and Møller⁸⁴ used straight lines to extrapolate the limiting curves of dissociation of CO, a procedure quite adequate to resolve the conundrum that they were addressing at the time (whether the BDE of CO is ~ 11 eV or nearly 2 eV lower; see, for example, the discussion in Gaydon⁸⁵) but too crude to extract $D_0(\text{CO})$ within their stated accuracy of $\pm 30 \text{ cm}^{-1}$. $D_0(\text{CO})$ of Douglas and Møller was the only reasonable choice for extracting $\Delta_f H^\circ(\text{C})$ that was available to the CODATA Task Group,²² because alternative measurements that could lead to this important quantity, such as high-temperature equilibria of C atom above graphite, are rendered too inaccurate by inherent experimental complexities. The suspicion that the CODATA value for $\Delta_f H^\circ(\text{C})$ may be somewhat underestimated, perhaps by as much as 0.5 kJ/mol, was additionally fueled by subsequent statistical arguments that were developed by comparing computed atomization energies to experimental enthalpies of formation for a series of hydrocarbons up to octane.⁸⁶

Since these early attempts to obtain a better handle on $\Delta_f H^\circ(\text{C})$ in spite of the “weak link” $D_0(\text{CO})$, the ATcT TN has gradually expanded by nearly 5-fold, and the number of determinations that include C atom eventually reached a “critical mass”, giving credence to the gradually converging ATcT value for $\Delta_f H^\circ(\text{C})$. While technically still provisional (pending a final analysis), the current ATcT value is sufficiently robust for the purposes of the present study: $\Delta_f H^\circ_{298}(\text{C}) = \Delta_f H^\circ_{298}(^{13}\text{C}) = 716.886 \pm 0.050 \text{ kJ/mol}$ (711.401 kJ/mol at 0 K) and $\Delta_f H^\circ_{298}(^{1}\text{C}) = 838.478 \pm 0.050 \text{ kJ/mol}$ (833.332 kJ/mol at 0 K). The current ATcT value for $\Delta_f H^\circ_{298}(\text{C})$ stays practically unchanged from the two prior ATcT updates, given in Stevens et al.¹⁷ ($716.87 \pm 0.06 \text{ kJ/mol}$, from ATcT TN ver. 1.110) and in Ruscic et al.¹⁹ ($716.880 \pm 0.054 \text{ kJ/mol}$, from ATcT TN ver. 1.118). Note that the ATcT value is moderately higher (by $\sim 0.20 \text{ kJ/mol}$), and significantly more accurate than the CODATA value ($716.68 \pm 0.45 \text{ kJ/mol}$ at 298.15 K).

The ATcT bond dissociation enthalpy of regular (and doublet-only) methylidyne to form regular (or triplet-only) C atom is $\text{BDE}_{298}(\text{CH}) = 338.77 \pm 0.10 \text{ kJ/mol}$ (334.65 kJ/mol at 0 K). Additional variants of $\text{BDE}(\text{CH})$, involving non-standard methylidyne and nonstandard C atom species, are as follows: regular (or doublet-only) methylidyne dissociating to singlet-only C atom produces $\text{BDE}_{298}(\text{CH}) = 460.36 \pm 0.10 \text{ kJ/mol}$ (456.58 kJ/mol at 0 K), quartet-only methylidyne dissociating to regular (triplet-only) C atom produces $\text{BDE}_{298}(\text{CH}) = 267.00 \pm 0.59 \text{ kJ/mol}$ (262.89 kJ/mol at 0 K), and quartet-only methylidyne dissociating to singlet-only C atom is $\text{BDE}_{298}(\text{CH}) = 388.60 \pm 0.59 \text{ kJ/mol}$ (384.82 kJ/mol at 0 K).

Summary of the Sequential BDEs in the CH_n System.

A complete set of all 298.15 and 0 K BDEs within the CH_n system, involving regular as well as nonstandard species, is given in Table 1. The 298.15 K values for the BDEs of methane, methyl, methylene, and methylidyne involving only regular species are usually taken as the normal presentation of the four sequential BDEs of methane, and are visually summarized in Figure 1. The BDE sequence follows a characteristic pattern, different than that found in the analogous SiH_n and GeH_n systems and commented on previously.^{58,71,72,87} The second sequential bond of CH_4 is stronger than the first (by $24.25 \pm 0.16 \text{ kJ/mol}$ at 298.15 K) and is, in

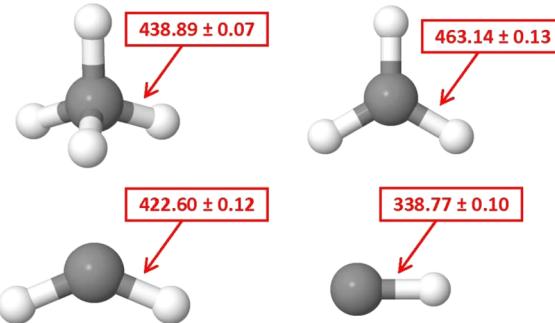


Figure 1. Sequential bond dissociation enthalpies of methane (in kJ/mol at 298.15 K).

fact, the strongest in the set; the third bond is weaker than either of the first two (by 16.29 ± 0.14 and $40.54 \pm 0.21 \text{ kJ/mol}$, respectively, at 298.15 K), and the last bond is by far the weakest of them all (weaker than the first three by 100.12 ± 0.12 , 124.37 ± 0.17 , and $83.83 \pm 0.19 \text{ kJ/mol}$, respectively, at 298.15 K). Of course, the four BDEs of CH_4 sum up to the total atomization enthalpy of methane, $\text{TAE}_{298}(\text{CH}_4) = 1663.397 \pm 0.067 \text{ kJ/mol}$ (1642.087 kJ/mol at 0 K).

The average bond enthalpy, BE_{av} , is a concept that was extensively used by Pauling^{5,88} to derive significant insights into the nature of chemical bonding and is still widely used in some areas of chemistry to obtain back-of-the-envelope estimates of reaction enthalpies. An unfortunate unintended consequence of this concept is that it creates, with the uninitiated, the impression that the four sequential bond enthalpies of methane are equal, which they obviously are not. The value for the average C–H bond enthalpy can be obtained from the total atomization enthalpy of methane as $\text{BE}_{\text{av}}(\text{C–H}) = \text{TAE}(\text{CH}_4)/4$, resulting in $\text{BE}_{\text{av},298}(\text{C–H}) = 415.849 \pm 0.017 \text{ kJ/mol}$. Clearly, $\text{BE}_{\text{av},298}(\text{C–H})$ is significantly lower than the thermochemically correct value for either of the first two BDEs of methane (by 23.043 and 47.29 kJ/mol, respectively), moderately lower (6.75 kJ/mol) than the third BDE, but very much higher (by 77.08 kJ/mol) than the fourth BDE.

ATcT Values for $\Delta_f H^\circ(\text{CH}_3\text{CH}_3)$ and $\text{BDE}(\text{CH}_3-\text{CH}_3)$. The ATcT enthalpy of formation of ethane is $\Delta_f H^\circ_{298}(\text{CH}_3\text{CH}_3) = -83.91 \pm 0.14 \text{ kJ/mol}$ (-68.29 kJ/mol at 0 K), nearly 3 times more accurate than the often quoted (and somewhat dissonant) 298.15 K values found in the NBS tables^{40,41} ($-84.68 \pm 0.40 \text{ kJ/mol}$), Pedley et al.³⁹ ($-83.8 \pm 0.4 \text{ kJ/mol}$), or Gurvich et al.²⁴ ($-84.0 \pm 0.4 \text{ kJ/mol}$).

The provenance of the ATcT enthalpy of formation of ethane is quite substantial, involving 432 determinations in the top 90% (2300 in the top 99%). The most prominent contributors include a number of calorimetric determinations, such as the combustion of ethane by Pittam and Pilcher⁴² (15.7%) and Rossini^{89,90} (1.9%), the combustion of ethylene by Rossini and Knowlton⁹¹ (3.7%), the combustion of propane by Pittam and Pilcher⁴² (2.0%), the hydrogenation of ethylene by Kistiakowsky et al.⁹² (6.0%), and the hydrogenation of acetylene by Conn et al.⁹³ (1.1%), as well as measurements of ethane–ethylene equilibria by Kistiakowsky and Nickle⁹⁴ (2.9% and 1.4%), together with Rossini’s calorimetry of hydrogen combustion^{45,51,52} (5.8%) and Smith’s⁵⁰ hydrogen/graphite/methane equilibrium (3.0%). The top two theoretical contributors are the computed values of the energies for the isodesmic reactions of $\text{CH}_3\text{CH}_2\text{CH}_3 + \text{CH}_4 \rightarrow 2 \text{CH}_3\text{CH}_3$ at the W4 level by Karton et al.^{79,95} (2.9%) and $\text{CH}_3\text{CCH} + \text{CH}_4$

$\rightarrow \text{CH}_3\text{CH}_3 + \text{HCCH}$ at the modified HEAT 345(Q) level by Ferguson^{96,97} (1.4%).

The ATcT values for the enthalpies of formation of ethane and methyl correspond to a C–C bond dissociation enthalpy $\text{BDE}_{298}(\text{CH}_3-\text{CH}_3) = 376.66 \pm 0.19 \text{ kJ/mol}$ (367.87 kJ/mol at 0 K), see Table 2. This BDE is often taken to represent the prototypical bond strength of a single C–C bond in hydrocarbons.

ATcT Values for $\Delta_f H^\circ(\text{CH}_3\text{CH}_2)$, $\text{BDE}(\text{CH}_3-\text{CH}_2)$, and $\text{BDE}(\text{H}-\text{CH}_2\text{CH}_3)$. The current ATcT enthalpy of formation of ethyl is $\Delta_f H^\circ_{298}(\text{CH}_3\text{CH}_2) = 119.86 \pm 0.28 \text{ kJ/mol}$ (130.92 kJ/mol at 0 K), which can be compared with the 298.15 K value from the evaluation of Tsang⁵⁷ ($119 \pm 2 \text{ kJ/mol}$), and the value selected by Lias et al.⁹⁸ (118 kJ/mol , from Cao and Back⁹⁹). The NBS tables^{40,41} ($107.5 \pm 4.0 \text{ kJ/mol}$) and Gurvich et al.²⁴ ($107 \pm 6 \text{ kJ/mol}$) list outdated and significantly lower values; a subsequent photoionization study of ethyl radical¹⁰⁰ has strongly suggested a significantly higher value ($\sim 119 \text{ kJ/mol}$ at 298.15 K) based on the measured IE_a(C₂H₅) and a range of values available at the time for ethylium, C₂H₅⁺. That was followed by kinetic studies that provided values hovering around 120–121 kJ/mol at 298.15 K, such as Seakins et al.¹⁰¹ ($121.0 \pm 1.5 \text{ kJ/mol}$) and Hanning-Lee et al.¹⁰² ($120.2 \pm 0.9 \text{ kJ/mol}$). A similar 298.15 K value ($120.7 \pm 1.1 \text{ kJ/mol}$) was produced in a more recent study by Bödi et al.¹⁰³ that applied the ATcT idea to a small localized TN constructed from pertinent photoionization data. Within their uncertainties, all of these recent values are clearly compatible with the ATcT value. Most recently, Leplat et al.¹⁰⁴ recommended a somewhat lower value ($117.3 \pm 3.1 \text{ kJ/mol}$), based on kinetic data obtained in a Knudsen flow reactor. However, one should note that their value has a sufficiently large uncertainty to produce an overlap with the current ATcT value.

The top 90% of the provenance of the ATcT value encompasses 374 determinations (1770 determinations for 99%); the top 16 contributors have contributions >1% each. The largest experimental contributors are the photoionization determination of the IE_a of ethyl by Ruscic et al.¹⁰⁰ (4.0%), the third law Gibbs energy of the reaction of ethyl with HBr, obtained by combining the kinetic studies of Dobis and Benson¹⁰⁵ with those of Seakins et al.,¹⁰¹ Nicovich et al.,¹⁰⁶ and King et al.¹⁰⁷ at 530 and 298 K (2.6% and 1.6%), the third and second law treatment of the kinetic studies of the same reaction by Ferrel¹⁰⁸ (1.8% each) and by Seakins et al.¹⁰¹ (1.4% each), the third law treatment of the kinetic data by Seetula¹⁰⁹ (1.3%), the second law treatment of combined kinetic data of Dobis and Benson¹⁰⁵ and Amphlett and Whittle¹¹⁰ (1.1%), and the third law treatment of the combined data of Dobis and Benson,¹⁰⁵ Seakins et al.,¹⁰¹ and Nicovich et al.¹⁰⁶ (1.1%). The top contributors also include the combustion calorimetry of ethane by Pittam and Pilcher⁴² (fourth largest contributor, 2.1%), the photoionization AE₀ of CH₃CH₂⁺ from ethyl bromide determined by Baer et al.¹¹¹ (1.5%), and the combustion calorimetry of hydrogen^{45,51,52} (1.1%). The three largest theoretical contributors are IE_a of ethyl computed by Lau and Ng¹¹² (3.8%) and the computations of the C–H bond enthalpy in ethane and of the enthalpy of the isodesmic reaction C₂H₅ + CH₄ → CH₃ + CH₃CH₃ by Marshal¹¹³ (1.2% and 1.1%), all computed at the CCSD(T)/CBS level with various additional corrections.

The ATcT value for the C–C bond dissociation of ethyl is $\text{BDE}_{298}(\text{CH}_3-\text{CH}_2) = 418.03 \pm 0.31 \text{ kJ/mol}$ (409.83 kJ/mol at 0 K) to form regular (or triplet-only) methylene, and $455.55 \pm$

0.31 kJ/mol (447.49 kJ/mol at 0 K) to form singlet-only methylene. Of note is the fact that the C–C bond of ethyl to form regular products is significantly stronger (by $41.37 \pm 0.29 \text{ kJ/mol}$ at 298.15 K) than the C–C bond in ethane.

The ATcT value for the C–H bond dissociation enthalpy of ethane is $\text{BDE}_{298}(\text{H}-\text{CH}_2\text{CH}_3) = 421.77 \pm 0.26 \text{ kJ/mol}$ (415.25 kJ/mol at 0 K), quite similar to the third BDE in methane (weaker by only $0.83 \pm 0.29 \text{ kJ/mol}$ at 298.15 K), moderately weaker than the first sequential BDE of methane (by $17.12 \pm 0.27 \text{ kJ/mol}$ at 298.15 K), and significantly weaker than the second BDE of methane (by $41.37 \pm 0.29 \text{ kJ/mol}$ at 298.15 K).

ATcT Values for $\Delta_f H^\circ(\text{CH}_2\text{CH}_2)$, $\text{BDE}(\text{CH}_2-\text{CH}_2)$, and $\text{BDE}(\text{H}-\text{CH}_2\text{CH}_2)$. The enthalpy of formation of ethylene is $\Delta_f H^\circ_{298}(\text{CH}_2\text{CH}_2) = 52.45 \pm 0.13 \text{ kJ/mol}$ (60.96 kJ/mol at 0 K). The often quoted 298.15 K values found in standard compilations, such as the NBS tables^{40,41} ($52.26 \pm 0.40 \text{ kJ/mol}$), JANAF tables²³ ($52.47 \pm 0.29 \text{ kJ/mol}$), and Gurvich et al.²⁴ ($52.4 \pm 0.5 \text{ kJ/mol}$), or Pedley et al.³⁹ ($52.5 \pm 0.4 \text{ kJ/mol}$) are entirely compatible but less accurate.

As in the other cases discussed so far, the provenance of $\Delta_f H^\circ(\text{CH}_2\text{CH}_2)$ is quite distributed: the top 90% includes 493 determinations, and 99% includes 2602 determinations. There are eight contributors with individual contributions of 2% or more. The largest is the combustion calorimetry of ethylene by Rossini and Knowlton⁹¹ (11.2%), together with the combustion calorimetry of hydrogen by Rossini^{95,51,52} (5.0%), combustion calorimetry of ethane by Pittam and Pilcher⁴² (4.9%), hydrogenation of ethylene by Kistiakowsky et al.⁹² (2.9%), the graphite/hydrogen/methane equilibrium by Smith⁵⁰ (2.8%), the Gibbs energy of the cyclobutane/ethane equilibrium by Quick et al.¹¹⁴ (2.7%), and the combustion calorimetry of ethyl chloride by Fletcher and Pilcher¹¹⁵ (2.0%). Besides these experimental measurements, one of the top eight contributors is from theory: the 0 K enthalpy of the reaction $\text{CH}_3\text{CCH} + \text{CH}_4 \rightarrow \text{CH}_3\text{CH}_3 + \text{HCCH}$ obtained at the modified HEAT 345(Q) level by Ferguson^{96,97} (2.4%).

The ATcT value for the enthalpy of dissociation of the C=C bond in ethylene is $\text{BDE}_{298}(\text{CH}_2-\text{CH}_2) = 730.59 \pm 0.24 \text{ kJ/mol}$ (720.96 kJ/mol at 0 K) to form regular or triplet-only methylene. Other variants of the carbon–carbon BDE ethylene, which refer to nonstandard species, are $\text{BDE}_{298}(\text{CH}_2-\text{CH}_2) = 805.62 \pm 0.26 \text{ kJ/mol}$ (796.28 kJ/mol at 0 K) to form ${}^1\text{CH}_2 + {}^1\text{CH}_2$, and $768.10 \pm 0.24 \text{ kJ/mol}$ (758.62 kJ/mol at 0 K) to form ${}^3\text{CH}_2 + {}^1\text{CH}_2$.

The carbon–carbon BDE in ethylene, forming regular methylene, is frequently taken to represent the prototypical double C=C bond. True to its name, it is nearly twice (1.9397 ± 0.0012 times) the value of the single carbon–carbon BDE in ethane. Parenthetically, the expectation that a π bond is very nearly as strong as a σ bond is applicable only in the first row of the periodic table; this ceases to be valid in the second and higher rows of the periodic table, since there—as bonds generally get progressively weaker in successive rows—the strength of π bonds tends to fall off more rapidly than the strength of σ bonds.^{72,116,117} Also, as we shall see later while discussing the triple C≡C bond in acetylene (*vide infra*), the second π bond is not necessarily as strong as the first π bond, even in the first row of the periodic table.

A hydrogen atom removal in ethyl can occur either on the CH₃ side or on the CH₂ side. The former leads to ethylene, and its ATcT value is $\text{BDE}_{298}(\text{H}-\text{CH}_2\text{CH}_2) = 150.59 \pm 0.27 \text{ kJ/mol}$ (146.08 kJ/mol at 0 K). This BDE is remarkably lower

than any of the C–H BDEs considered so far, and *prima facie* may appear pathological. The reason for the very low value is, of course, that the enthalpy expenditure for the removal of the hydrogen atom is partially compensated by a concurrent increase in the stability of the carbon–carbon bond, from an essentially single C–C bond in ethyl to a double C=C bond in ethylene. To illustrate quantitatively the effects at play, let us for a moment imagine that Maxwell's demon were able to arrange this dissociation to occur in two distinct phases, while still preserving the first law of thermodynamics for the overall process. In this scenario, the first phase would correspond to the removal of the hydrogen atom from the CH₃ side of ethyl while keeping the C–C bond frozen at its original strength, and the second phase would correspond to a relaxation of the frozen C–C bond to a C=C bond appropriate for ethylene. If such an arrangement were possible, the second phase would have to return back BDE₂₉₈(CH₂–CH₂) – BDE₂₉₈(CH₃–CH₂) = 312.55 ± 0.29 kJ/mol. In order to preserve the first law, the enthalpy expenditure during the first phase would have to be BDE₂₉₈(H–CH₂CH₂) + 312.55 kJ/mol = 463.14 kJ/mol, which exactly corresponds (as it must¹¹⁸) to the second BDE in methane.

ATcT Values for Δ_fH°(CH₃CH), BDE(CH₃–CH), and BDE(CH₃CH–H). Ethylidene, CH₃CH, is the carbene isomer of ethylene. It corresponds to methyl-substituted methylene, and, just like methylene, its ground state is a triplet. Ethylidene is in ATcT represented as three species: regular ethylidene (^{eq}CH₃CH or CH₃CH), triplet ethylidene (³CH₃CH), and singlet ethylidene (¹CH₃CH). The current ATcT enthalpy of formation of regular ethylidene is Δ_fH°₂₉₈(CH₃CH) = 354.47 ± 0.82 kJ/mol (361.45 kJ/mol at 0 K), and the corresponding values for the triplet-only and singlet-only counterparts are Δ_fH°₂₉₈(³CH₃CH) = 354.45 ± 0.82 kJ/mol (361.45 kJ/mol at 0 K) and Δ_fH°₂₉₈(¹CH₃CH) = 366.70 ± 0.86 kJ/mol (373.93 kJ/mol at 0 K). Given the transient nature of this isomer, it is not particularly surprising that its thermochemistry is absent from traditional tabulation.

Considering the paucity of data on ethylidene, the provenance of its ATcT enthalpy of formation is pleasingly well distributed: for the regular and the triplet-only species, the top 90% of the provenance is spread over 50 determination (312 for 99%), and similarly for the singlet-only species (49 for 90%, 304 for 99%). Not surprisingly, the dominant contributions come from theoretical determinations. For regular and triplet-only ethylidene, the top two contributions come from the FPD treatment of Nguyen et al.¹¹⁹ in the form of the 0 K enthalpy difference between triplet ethylidene and ethylene (5.7%) and TAE₀ of ethylidene (4.5%), followed by several in-house computational results, such as the 0 K enthalpy for the isodesmic reactions ³CH₃CH + CH₄ → ³CH₂ + CH₃CH₃ (4.3%), and ³CH₃CH + CH₃ → ³CH₂ + CH₃CH₂ (4.1%) at the W1 level, and the same reactions at the G4 level (3.5 and 3.3%), CBS-APNO level (3.5 and 3.3%), G3X level (2.9 and 2.7%), G3 level (2.4 and 2.3%), G3B3 level (2.4 and 2.3%), and CBS-QB3 level (2.1 and 2.0%), and the 0 K triplet ethylidene–ethylene excitation energy at the W1 level (2.5%), G4 level (2.1%) and CBS-APNO level of theory (2.1%). Beyond these, the individual contributions fall below the 2% mark; nevertheless, it is worthwhile to mention two more determinations from the literature: the 0 K triplet ethylidene–ethylene excitation energy and the triplet-singlet separation in ethylidene from CCL/CBS calculations by Ge and Shore¹²⁰ (1.8 and 1.0%), and the 0 K enthalpy of the isodesmic reaction

³CH₃CH + CH₃ → ³CH₂ + CH₃CH₂ at the CCSD(T)/CBS level with corrections for CI truncation from Yu and Muckerman¹²¹ (1.5%). The main contributors to the enthalpy of formation of singlet-only ethylidene are analogous versions of in-house computational results that involve the singlet state.

The ATcT value for the C–C bond dissociation enthalpy in ethylidene is BDE₂₉₈(CH₃–CH) = 388.02 ± 0.82 kJ/mol (381.12 kJ/mol at 0 K) to form regular or doublet-only methylidyne. This BDE is stronger (by 11.36 ± 0.81 kJ/mol at 298.15 K) than the C–C BDE in ethane, but weaker (30.01 ± 0.84 kJ/mol at 298.15 K) than the C–C BDE in ethyl. The variant of the C–C BDE in ethylidene that results in quartet-only methylidyne is BDE₂₉₈(CH₃–CH) = 459.78 ± 1.00 kJ/mol (452.88 kJ/mol at 0 K). Other variants of BDE(CH₃–CH), involving triplet-only and singlet-only ethylidene and regular and nonstandard methylidyne are given in Table 2.

The ATcT C–H bond dissociation enthalpy from the CH₂ side in ethyl, which leads to regular ethylidene, is BDE₂₉₈(CH₃CH–H) = 452.61 ± 0.82 kJ/mol (446.57 kJ/mol at 0 K); other variants, which result in triplet-only or singlet-only ethylidene, are given in Table 2. As opposed to the nearly exactly three times weaker C–H BDE on the CH₃ side of ethyl, the C–H BDE on the CH₂ side is significantly closer to a normal C–H bond. A more careful quantitative comparison¹²² shows that the concurrent weakening of the carbon–carbon bond in going from ethyl to ethylidene (by 30.01 ± 0.84 kJ/mol at 298.15 K) causes BDE(CH₃CH–H) to be stronger than the C–H BDE in methylene by the same amount.

ATcT Values for Δ_fH°(CH₂CH), BDE(CH₂–CH), BDE(H–CHCH₂), and BDE(H–CH₂CH). The ATcT enthalpy of formation of vinyl is Δ_fH°₂₉₈(CH₂CH) = 296.91 ± 0.33 kJ/mol (301.11 kJ/mol at 0 K). Gurvich et al.²⁴ list a significantly lower value, 260 ± 10 kJ/mol at 298.15 K, while JANAF²³ does not list this species at all. A subsequent photoionization study of vinyl by Berkowitz et al.¹²³ has established the likely lower and upper limits to D₀(CH₂CH–H), implying that Δ_fH°₂₉₈(CH₂CH) is in the range of ~288–301 kJ/mol, noticeably higher than the value found in Gurvich et al. The values selected in the evaluations by Tsang⁵⁷ (299 ± 5) and Berkowitz et al.⁵⁸ (299.6 ± 3.3 kJ/mol) are indeed higher and compatible with the current ATcT result within their significantly larger uncertainties.

The provenance of the ATcT enthalpy of formation of vinyl is quite distributed, involving 162 determination in the top 90% and 1304 determinations in the top 99%. There are 12 determinations with individual contributions of 2% or more. The top contributor (7.0%) is the third law analysis of the equilibrium CH₂CH₂ + Cl → CH₂CH + HCl, based on kinetic measurements of Kaiser and Wallington¹²⁴ and Russell et al.¹²⁵ Other top contributors, ranging individually between 5.9% and 2.0%, are extracted from state-of-the-art theoretical computations obtained at the HEAT 345-(Q) level of theory by Tabor et al.,¹²⁶ at the W4 and W4.2 level of theory by Karton et al.,^{68,76,79} and at the CCSD(T)-R12 level of theory by Aguilera-Iparraguirre et al.,⁷⁷ and inserted in the TN as TAE₀(CH₂CH), D₀(CH₂CH–H), D₀(H–CHCH), D₀(CH₂C–H), and D(CH₂CH–O).

The ATcT dissociation enthalpy of the carbon–carbon bond in vinyl to form regular products is BDE₂₉₈(CH₂–CH) = 690.72 ± 0.36 kJ/mol (682.63 kJ/mol at 0 K), noticeably weaker (by 39.87 ± 0.34 kJ/mol at 298.15 K) than the C=C BDE in ethylene, though still significantly stronger (by 314.06

± 0.39 kJ/mol at 298.15 K) than the single C–C BDE in ethane. Four additional variants of $\text{BDE}_{298}(\text{CH}_2\text{—CH})$, which produce various combinations of nonstandard methylene and methylidyne species, are given in Table 2.

The C–H bond dissociation in ethylene leads to vinyl, and its ATcT enthalpy is $\text{BDE}_{298}(\text{H—CHCH}_2) = 462.46 \pm 0.33$ kJ/mol (456.18 kJ/mol at 0 K). This bond is noticeably stronger (by 40.69 ± 0.41 kJ/mol at 298.15 K) than the prototypical C–H bond in ethane, since the removal of a hydrogen from ethylene concurrently causes weakening of the carbon–carbon bond. In the Maxwell's demon scenario, the second phase, which brings the frozen C=C bond in ethylene to its proper strength in vinyl, would incur an enthalpy cost of $\text{BDE}_{298}(\text{CH}_2\text{—CH}_2) - \text{BDE}_{298}(\text{CH}_2\text{—CH}) = 39.87 \pm 0.34$ kJ/mol, and thus the first phase, which removes a hydrogen while keeping the C=C bond in ethylene frozen, would cost only 422.60 kJ/mol at 298.15 K, exactly as much as the third BDE in methane.¹²⁷

The C–H bond dissociation on the CH₃ side of ethylidene also leads to vinyl. The ATcT value for this bond dissociation enthalpy is $\text{BDE}_{298}(\text{H—CH}_2\text{CH}) = 160.44 \pm 0.87$ kJ/mol (155.69 kJ/mol at 0 K). This bond is clearly much weaker than a normal C–H BDE, on account of the fact that the removal of a hydrogen from the CH₃ side of CH₃CH is accompanied by a simultaneous strengthening of the carbon–carbon bond, from an essentially single bond in ethylidene to an essentially double bond in vinyl. Invoking again the Maxwell's demon, the second step would return back $\text{BDE}_{298}(\text{CH}_2\text{—CH}) - \text{BDE}(\text{CH}_3\text{—CH}) = 302.70 \pm 0.89$ kJ/mol, and thus the first step, corresponding to a removal of hydrogen without upsetting the carbon–carbon bond, would cost 463.14 kJ/mol at 298.15 K, exactly as much¹²⁸ as the second BDE in methane.

ATcT Values for $\Delta_f H^\circ(\text{CH}_3\text{C})$, $\text{BDE}(\text{CH}_3\text{—C})$, and $\text{BDE}(\text{CH}_3\text{C—H})$. Ethylidyne is the high-energy isomer of vinyl, and corresponds to methyl-substituted methylidyne. As in the case of methylidyne, ethylidyne is in ATcT represented as three species: regular ethylidyne (CH₃C or ^{eq}CH₃C), doublet-only ethylidyne (²CH₃C), and quartet-only ethylidyne (⁴CH₃C). The ground electronic state of ethylidyne is a doublet, thus $\Delta_f H^\circ(\text{CH}_3\text{C}) \equiv \Delta_f H^\circ(\text{CH}_3\text{C})$. As encountered before in several other cases, $\Delta_f H^\circ_{298}(\text{CH}_3\text{C}) \cong \Delta_f H^\circ_{298}(\text{CH}_3\text{C})$ for all practical purposes, although at higher temperatures $\Delta_f H^\circ_T(\text{CH}_3\text{C}) \neq \Delta_f H^\circ_T(\text{CH}_3\text{C})$. The ATcT enthalpy of formation of ethylidyne is $\Delta_f H^\circ_{298}(\text{CH}_3\text{C}) = \Delta_f H^\circ_{298}(\text{CH}_3\text{C}) = 504.88 \pm 0.87$ kJ/mol (508.58 kJ/mol at 0 K), and $\Delta_f H^\circ_{298}(\text{CH}_3\text{C}) = 636.07 \pm 1.20$ kJ/mol (640.62 kJ/mol at 0 K). Not surprisingly, standard compilations do not list this species.

The provenance of the enthalpy of formation of ethylidyne is reasonably distributed, and includes 43 determinations in the top 90%, growing to 326 in the top 99%. The top 20 contributors have individual contributions between 5.0 and 2.0%. Ethylidyne suffers from a pronounced paucity of data, perhaps even more than ethylidene. Consequently, the top contributors are determinations that are extracted from in-house composite electronic structure computations at the W1, G4, CBS-APNO, and CBS-QB3 levels of theory, such as the isodesmic reactions $\text{CH}_3\text{C} + \text{CH}_4 \rightarrow \text{CH} + \text{CH}_3\text{CH}_3$ and $\text{CH}_3\text{C} + \text{CH}_3 \rightarrow \text{CH} + \text{CH}_3\text{CH}_2$ (where ethylidyne and methylidyne are both either in their doublet states or quartet states), the excitation energy of CH₃C above CH₃CH, the quartet-doublet separation in ethylidyne, the IE_a of ethylidyne, and the isogyric reaction $\text{CH}_3\text{C} + \text{H}_2 \rightarrow \text{CH} + \text{CH}_4$. A few

theoretical results found in the literature^{121,129} were also included in the TN, but none of these appear among the top 20 contributors.

The ATcT value for the carbon–carbon bond dissociation enthalpy of regular ethylidyne, producing a regular C atom, is $\text{BDE}_{298}(\text{CH}_3\text{—C}) = 358.38 \pm 0.87$ kJ/mol (352.61 kJ/mol at 0 K), somewhat weaker (by 18.28 ± 0.87 kJ/mol at 298.15 K) than the single C–C BDE in ethane, and noticeably weaker (by $29.6_4 \pm 1.1_8$ kJ/mol at 298.15 K) than the C–C BDE in ethylidene. The other variants of the C–C BDE of ethylidyne, which iterate through various combinations involving non-standard C atom species as well as nonstandard ethylidyne species are listed in Table 2 and will not be separately discussed here.

The C–H bond dissociation enthalpy on the CH side of regular ethylidene, leading to regular ethylidyne, is $\text{BDE}_{298}(\text{CH}_3\text{C—H}) = 368.4_1 \pm 1.1_8$ kJ/mol (363.1₆ kJ/mol at 0 K), considerably weaker (by $53.3_6 \pm 1.2_0$ kJ/mol at 298.15 K) than the C–H BDE in ethane. As above, the other variants of $\text{BDE}(\text{CH}_3\text{C—H})$, which consider nonstandard ethylidyne and/or ethylidene are given in Table 2 and will not be separately discussed. Of interest here is that the relative weakness of this C–H bond is *not* caused by a concomitant change in the C–C bond. To the contrary, the concurrent change in carbon–carbon bonding, if anything, helps to slightly strengthen this BDE. Namely, if the Maxwell's demon is invoked again, the second phase of the process, which restores the C–C bond from its strength frozen at the ethylidene level to the strength appropriate to ethylidyne, costs $29.6_4 \pm 1.1_8$ kJ/mol in additional enthalpy, since the final C–C bond is weaker than the starting C–C bond. Thus, the enthalpy cost during the first phase would, in fact, be even lower, 338.7₇ kJ/mol at 298.15 K, exactly equal¹³⁰ to $\text{BDE}(\text{CH})$. Thus, the primary reason for the comparative weakness of $\text{BDE}(\text{CH}_3\text{C—H})$ is that it is analogous to $\text{BDE}(\text{CH})$, the weakest sequential bond in methane.

ATcT Values for $\Delta_f H^\circ(\text{HCCH})$, $\text{BDE}(\text{HC—CH})$, and $\text{BDE}(\text{H—CHCH})$. The ATcT enthalpy of formation of acetylene is $\Delta_f H^\circ_{298}(\text{HCCH}) = 228.27 \pm 0.13$ kJ/mol (228.84 kJ/mol at 0 K). It is significantly more accurate than the often quoted values found in Pedley et al.³⁹ (228.2 ± 0.7 kJ/mol at 298.15 K), Gurvich et al.²⁴ (227.4 ± 0.8 kJ/mol at 298.15 K), JANAF tables²³ (226.73 ± 0.79 kJ/mol at 298.15 K), or NBS tables^{40,41} (226.73 ± 0.40 kJ/mol at 298.15 K), which, in addition, appear surprisingly discordant.

As expected, the provenance of the ATcT enthalpy of formation of acetylene is very distributed, with 563 contributors needed to pedigree 90% of the provenance, and 3108 contributors to pedigree 99%. Many of the top contributors do not involve HCCH directly (such as the combustion calorimetry of hydrogen,^{45,51,52} ethane,⁴² ethylene,⁹¹ hydrogen/graphite/methane equilibria,⁵⁰ graphite/carbon dioxide/carbon monoxide equilibria,⁵⁰ etc.), indicating that ATcT obtains the value of $\Delta_f H^\circ(\text{HCCH})$ from a large number of thermochemical cycles. Whether directly involving HCCH or not, the individual contributions are rather small (most of them less than 1%), dispersing the pedigree rather evenly over a large number of both experimental and theoretical determinations. The determinations that involve HCCH in a more direct manner and have individual contributions of 1% or more are AE₀ of HCCH⁺ from ethylene by Malow et al.¹³¹ (1.6%) and by Mähnert et al.¹³² (1.6%), D₀(H—CCH) by Mordaunt and Ashfold¹³³ (1.3%), hydrogenation of acetylene by Conn et al.⁹³

(1.0%), TAE₀(HCCCH) at the HEAT 345-QP level by Harding et al.⁵⁴ (1.4%) and at the W4.4 level by Karton et al.⁵³ (1.1%), TAE₀(CCH) at the HEAT 345-QP level⁵⁴ (1.0%), $\Delta_f H^\circ_0$ for the hydrogenation of acetylene to produce ethylene at the HEAT 345-(Q) level by Harding et al.¹³⁴ (1.0%), or to produce ethane at the W4 level by Karton et al.¹³⁵ (1.0%).

The ATcT value for the carbon–carbon bond dissociation enthalpy of acetylene to produce regular methylidyne is $BDE_{298}(\text{HC}-\text{CH}) = 963.96 \pm 0.21 \text{ kJ/mol}$ (956.73 kJ/mol at 0 K); other variants of this BDE, involving nonstandard methylidyne are given in Table 2. This BDE is often taken to represent the prototypical triple C≡C bond in hydrocarbons. Its value is 2.55923 ± 0.00055 times larger than the single C–C BDE in ethane. Taking the carbon–carbon σ bond in ethane as the basic unit, one notices that in going from ethane to ethylene the π bond adds 0.940 units to the carbon–carbon bond strength (*vide supra*), but in going from ethylene to acetylene, the second π bond adds only 0.620 units, the net effect of which is that the triple C≡C bond in acetylene is not 3 times but only 2.559 times the strength of a single C–C bond.

The ATcT value for the C–H BDE on the CH₂ side of vinyl is $BDE_{298}(\text{H}-\text{CHCH}) = 149.36 \pm 0.32 \text{ kJ/mol}$ (143.76 kJ/mol at 0 K), much lower than one would expect for a normal C–H bond. As in the previously discussed cases of $BDE(\text{H}-\text{CH}_2\text{CH}_2)$ and $BDE(\text{H}-\text{CH}_2\text{CH})$, the relevant effect in lowering the value of $BDE(\text{H}-\text{CHCH})$ is the concomitant strengthening of the carbon–carbon bond from the nearly double bond in vinyl to a triple bond in acetylene. In the Maxwell's demon scenario, the second phase would return $BDE_{298}(\text{HC}-\text{CH}) - BDE_{298}(\text{CH}_2-\text{CH})$, or $273.24 \pm 0.35 \text{ kJ/mol}$ of enthalpy, and thus the first phase would cost $BDE_{298}(\text{H}-\text{CHCH}) + [BDE_{298}(\text{HC}-\text{CH}) - BDE_{298}(\text{CH}_2-\text{CH})] = 422.60 \text{ kJ/mol}$, exactly as much as the BDE of methylene.¹³⁶

ATcT Values for $\Delta_f H^\circ(\text{CH}_2\text{C})$, Acetylene/Vinylidene Isomerization Enthalpy, $BDE(\text{CH}_2-\text{C})$, $BDE(\text{CH}_2\text{C}-\text{H})$, and $BDE(\text{H}-\text{CH}_2\text{C})$. Vinylidene is the high-energy isomer of acetylene. Its ATcT enthalpy of formation is $\Delta_f H^\circ_{298}(\text{CH}_2\text{C}) = 412.20 \pm 0.33 \text{ kJ/mol}$ (411.29 kJ/mol at 0 K). Standard compilation generally do not list this species.

The provenance of the enthalpy of formation of vinylidene is reasonably well distributed, since it takes 104 determinations to pedigree 90% of the provenance, and 1043 to pedigree 99%. The contributors are predominantly from theory. Earlier on, the thermochemistry of vinylidene was constrained in the TN by a number of determinations extracted from high-level theory, such as the acetylene–vinylidene isomerization energy at the CCSD(T)/CBS level (including additional higher-level corrections) by Stanton and Gauss,¹³⁷ Nguyen et al.,¹¹⁹ and Chang et al.¹³⁸ As newer and even more accurate theoretical data became available, these slightly older computations were gradually pushed down the list of top contributors, and in the current lineup the lead contributor is the recently published acetylene–vinylidene isomerization energy of Lee et al.¹³⁹ obtained at the state-of-the-art HEAT 456QP level of theory (19.7%). This is followed by the determinations at the W4.2 and W4 levels of theory of the acetylene–vinylidene isomerization energy (7.1% each) and of TAE₀(CH₂C) (5.5% each), obtained by Karton et al.^{68,76,79}

The current ATcT value for the isomerization energy is $182.45 \pm 0.31 \text{ kJ/mol}$ ($15252 \pm 26 \text{ cm}^{-1}$) at 0 K, corresponding to an enthalpy difference of 183.92 kJ/mol at 298.15 K. The ATcT isomerization energy is $\sim 270 \text{ cm}^{-1}$ below

the strict experimental upper limit of 15525 cm^{-1} established by Chen et al.¹⁴⁰ The quite recently computed theoretical value of $15224 \pm 52 \text{ cm}^{-1}$ by Lee et al.,¹³⁹ as well as the values of $182.5 (\pm 1) \text{ kJ/mol}$ by Karton et al.⁶⁸ and $15199 \pm 205 \text{ cm}^{-1}$ by Stanton and Gauss,¹³⁷ are in excellent agreement with the ATcT value, while the recent calculation by Joseph and Varandas,¹⁴¹ yielding $179.3 \pm 1.7 \text{ kJ/mol}$, appears too low. Prior, slightly less accurate theoretical results, such as $184.4 \pm 3.3 \text{ kJ/mol}$ by Nguyen et al.,¹¹⁹ $180 (\pm 4) \text{ kJ/mol}$ by Chang et al.,¹³⁸ $180 \pm 8 \text{ kJ/mol}$ by Gallo et al.,¹⁴² or 14708 cm^{-1} from the potential energy surface of Zou and Bowman,^{143,144} are also either in good or in reasonable agreement with the ATcT value.

The ATcT value for the carbon–carbon BDE in vinylidene, producing regular methylene and C atom, is $BDE_{298}(\text{CH}_2-\text{C}) = 696.20 \pm 0.33 \text{ kJ/mol}$ (691.08 kJ/mol at 0 K). Table 2 lists the other variants of this BDE that include various combinations of nonstandard species in the dissociation asymptote. As expected, this BDE is significantly weaker than the C≡C bond in acetylene (by $267.76 \pm 0.36 \text{ kJ/mol}$ at 298.15 K), and is noticeably weaker than the C=C bond in ethylene (by $34.39 \pm 0.34 \text{ kJ/mol}$ at 298.15 K), though it is very slightly stronger than the C=C bond in vinyl (by $5.48 \pm 0.42 \text{ kJ/mol}$ at 298.15 K).

The ATcT value for the C–H bond on the CH side of vinyl is $BDE_{298}(\text{CH}_2\text{C}-\text{H}) = 333.29 \pm 0.40 \text{ kJ/mol}$ (326.21 kJ/mol at 0 K). Although this is more than double the C–H BDE on the other, CH₂ side of vinyl, it is still considerably weaker than the C–H bond in ethylene (by $129.17 \pm 0.66 \text{ kJ/mol}$ at 298.15 K) or even in ethane (by $88.48 \pm 0.49 \text{ kJ/mol}$ at 298.15 K). As in the case of $BDE(\text{CH}_3\text{C}-\text{H})$, the primary reason for the relative weakness of this bond is that it is comparable¹⁴⁵ to $BDE(\text{CH})$, the weakest bond in the CH_n system, and only a very small amount ($5.48 \pm 0.42 \text{ kJ/mol}$ at 298.15 K) is associated with the concomitant strengthening of the carbon–carbon bond.

The ATcT value for the C–H BDE of ethylidyne is $BDE_{298}(\text{H}-\text{CH}_2\text{C}) = 125.31 \pm 0.92 \text{ kJ/mol}$ (118.74 kJ/mol at 0 K); other variants of this BDE, involving nonstandard reactants and products, are listed in Table 2. Analogous to other cases involving remarkably weak C–H bonds that were discussed thus far, the apparent anomaly can be fully rationalized by the concomitant gain in the carbon–carbon bond strength—by a whopping $337.82 \pm 0.93 \text{ kJ/mol}$ at 298.15 K—in going from ethylidyne to vinylidene. In the familiar Maxwell's demon scenario, the enthalpy cost during the first phase would be 463.14 kJ/mol at 298.15 K, exactly equal¹⁴⁶ to $BDE(\text{H}-\text{CH}_2)$.

ATcT Values for $\Delta_f H^\circ(\text{HCC})$, $BDE(\text{HC}-\text{C})$, $BDE(\text{H}-\text{CCH})$, and $BDE(\text{H}-\text{CHC})$. The ATcT enthalpy of formation of ethynyl is $\Delta_f H^\circ_{298}(\text{HCC}) = 567.99 \pm 0.15 \text{ kJ/mol}$ (563.87 kJ/mol at 0 K), significantly more accurate than the older but otherwise compatible value of Gurvich et al.²⁴ ($568.5 \pm 5.0 \text{ kJ/mol}$ at 298.15 K). JANAF²³ provides an entirely outdated and incompatible value ($477 \pm 29 \text{ kJ/mol}$ at 298.15 K). The evaluation of Berkowitz et al.⁵⁸ selects a value ($565.3 \pm 2.9 \text{ kJ/mol}$ at 298.15 K) based on photoionization measurements by Ruscic and Berkowitz¹⁴⁷ and on the negative ion cycle of Ervin et al.¹⁴⁸ The evaluation of Tsang⁵⁷ lists the outdated value from the 1992 JPL compilation¹⁴⁹ ($556 \pm 8 \text{ kJ/mol}$ at 298.15 K, which was subsequently changed¹⁵⁰ to the value from Berkowitz et al.⁵⁸).

The provenance of $\Delta_f H^\circ(\text{HCC})$ is very distributed, with 489 determinations necessary to pedigree the top 90% of the

provenance, and 2871 for 99%. As in the case of acetylene, many of the top contributors do not involve HCCH directly, indicating extensive use of various thermochemical cycles. Except for several contributors at the top, the individual contributions rather quickly dwindle down to the sub-2% level. The top contributor is the experimental determination of $D_0(\text{H-CCH})$ by Mordaunt and Ashfold¹³³ (11.3%). Among the other determinations that directly involve HCC, the two most prominent contributors are from theory: TAE₀ at the HEAT 345-QP and HEAT 345-(Q) levels of theory by Harding et al.⁵⁴ (2.1 and 1.4%) and at the W4 level by Karton et al.⁶⁸ (1.7%). In general, many contributors are the same as in the case of acetylene, reflecting the significant correlation ($r_{\text{HCCH}, \text{HCC}} = 0.84253$) between the two enthalpies of formation.

The ATcT value for the carbon–carbon BDE of ethynyl, resulting in regular methylidyne and C atom, is $\text{BDE}_{298}(\text{CH}-\text{C}) = 745.02 \pm 0.15 \text{ kJ/mol}$ (740.31 kJ/mol at 0 K); variants involving nonstandard versions of the dissociation products are given in Table 2. This BDE is much weaker (by $218.94 \pm 0.12 \text{ kJ/mol}$ at 298.15 K) than the C≡C BDE in acetylene, but significantly stronger ($48.82 \pm 0.33 \text{ kJ/mol}$ at 298.15 K) than the carbon–carbon BDE in vinylidene, and marginally stronger ($14.43 \pm 0.25 \text{ kJ/mol}$ at 298.15 K) than the C=C BDE in ethylene.

The C–H BDE in acetylene is $\text{BDE}_{298}(\text{H-CCH}) = 557.709 \pm 0.078 \text{ kJ/mol}$ (551.072 kJ/mol at 0 K). It is the strongest C–H bond examined so far, part of its strength coming from the concomitant weakening of the carbon–carbon bond from a triple bond in acetylene to an essentially double bond in ethynyl. In the Maxwell's demon scenario, the second phase of the dissociation would cost—as discussed above—an additional $218.94 \pm 0.12 \text{ kJ/mol}$ in enthalpy at 298.15 K, and thus the first phase would cost only 338.77 kJ/mol at 298.15 K, equivalent¹⁵¹ to $\text{BDE}(\text{CH})$.

The C–H BDE in vinylidene is $\text{BDE}_{298}(\text{H-CHC}) = 373.78 \pm 0.32 \text{ kJ/mol}$ (368.62 kJ/mol at 0 K). This bond is considerably weaker (by $47.99 \pm 0.41 \text{ kJ/mol}$) than the bellwether C–H BDE in ethane. The weakness is related to the concomitant increase (by $48.82 \pm 0.33 \text{ kJ/mol}$ at 298.15 K) in the strength of the carbon–carbon bond in going from vinylidene to ethynyl. In the Maxwell's demon scenario, the first phase would cost 422.60 kJ/mol at 298.15 K, equivalent¹⁵² to $\text{BDE}(\text{H-CH})$.

ATcT Values for $\Delta_f H^\circ(\text{C}_2)$, $\text{BDE}(\text{C-C})$, and $\text{BDE}(\text{H-CC})$. Ethynylene is represented in ATcT as three species: regular ethynylene (^{eq}C₂ or simply C₂), singlet-only ethynylene (¹C₂), and triplet-only ethynylene (³C₂). The ground state of C₂ is ¹Σ_g⁺, and thus $\Delta_f H^\circ_0(\text{C}_2) \equiv \Delta_f H^\circ_0(^1\text{C}_2)$, but $\Delta_f H^\circ_{298}(\text{C}_2) \neq \Delta_f H^\circ_{298}(^1\text{C}_2)$. The ATcT enthalpy of formation of ethynylene is $\Delta_f H^\circ_{298}(\text{C}_2) = 828.68 \pm 0.27 \text{ kJ/mol}$ (820.21 kJ/mol at 0 K), $\Delta_f H^\circ_{298}(^1\text{C}_2) = 826.78 \pm 0.27 \text{ kJ/mol}$ (820.21 kJ/mol at 0 K), $\Delta_f H^\circ_{298}(^3\text{C}_2) = 834.08 \pm 0.27 \text{ kJ/mol}$ (827.38 kJ/mol at 0 K). The current value for regular ethynylene is practically identical to the previously published ATcT value¹⁹ ($828.73 \pm 0.29 \text{ kJ/mol}$ at 298.15 K) obtained from the earlier version of the ATcT TN. Not surprisingly—given the lack of reliable experimental data¹⁹—the values found in standard compilations, such as JANAF²³ ($837.7 \pm 3.8 \text{ kJ/mol}$ at 298.15 K), Gurvich et al.²⁴ ($830.5 \pm 10.0 \text{ kJ/mol}$ at 298.15 K), and NBS^{40,41} ($831.90 \pm 0.40 \text{ kJ/mol}$ at 298.15 K), are not particularly dependable.

The provenance of the ATcT value for $\Delta_f H^\circ(\text{C}_2)$ has been recently discussed,¹⁹ together with the relative roles of

experimental and theoretical data on C₂. Since the previous version of the TN, the only change of relevance for C₂ was the additional insertion of benchmark-quality $D_0(\text{C}_2)$ that was obtained at the limit of current computational capabilities by the FPD approach.⁷³ Needless to say, that determination now ranks as one of the top three contributors to the provenance of $\Delta_f H^\circ(\text{C}_2)$.

The ATcT value for the bond dissociation enthalpy of ethynylene is $\text{BDE}_{298}(\text{C}_2) = 605.10 \pm 0.25 \text{ kJ/mol}$ (602.59 kJ/mol at 0 K). Other version of this BDE, involving nonstandard ethynylene and nonstandard C atom species are listed in Table 2. The bond in ethynylene most certainly does not thermodynamically qualify as a triple bond—it is significantly weaker (by $358.86 \pm 0.31 \text{ kJ/mol}$ at 298.15 K) than the triple C≡C bond in acetylene. In fact, it is even weaker than any other double C=C bond in the C₂H_n system, such as ethylene (by $125.49 \pm 0.34 \text{ kJ/mol}$ at 298.15 K), vinyl (by $85.62 \pm 0.43 \text{ kJ/mol}$ at 298.15 K), vinylidene (by $91.10 \pm 0.41 \text{ kJ/mol}$ at 298.15 K), or ethynyl (by $139.92 \pm 0.28 \text{ kJ/mol}$ at 298.15 K), though it is evidently stronger than any other single C–C bond in the C₂H_n system, such as ethane (by $228.44 \pm 0.31 \text{ kJ/mol}$ at 298.15 K), ethyl (by $187.07 \pm 0.39 \text{ kJ/mol}$ at 298.15 K), ethylidene (by $217.08 \pm 0.86 \text{ kJ/mol}$ at 298.15 K), or ethylidyne (by $246.72 \pm 0.91 \text{ kJ/mol}$ at 298.15 K). From a purely thermodynamic point of view, one can decisively say that the bond strength in C₂ is more than a single C–C bond, but less than a double C=C bond. In fact, based on current ATcT values, the ratio $\text{BDE}_{298}(\text{C}_2)/\text{BDE}_{298}(\text{CH}_3\text{CH}_3)$ can be obtained quite accurately, and amounts to 1.6065 ± 0.0011 .

The ATcT value for the C–H BDE in ethynyl is $\text{BDE}_{298}(\text{H-CC}) = 478.69 \pm 0.26 \text{ kJ/mol}$ (472.37 kJ/mol at 0 K). This bond is considerably stronger than the prototypical C–H BDE in ethane (by $56.92 \pm 0.37 \text{ kJ/mol}$ at 298.15 K). The excess enthalpy can be rationalized by the concomitant weakening of the carbon–carbon bond in going from ethynyl to ethynylene (by $139.92 \pm 0.28 \text{ kJ/mol}$ at 298.15 K). In the Maxwell's demon scenario, the first step would costs only 338.77 kJ/mol at 298.15 K, which, as expected, exactly¹⁵³ corresponds to $\text{BDE}_{298}(\text{CH})$.

Summary of the Sequential BDEs in the C₂H_n System.

The 298.15 K values for all possible C–H and C–C BDEs of ethane, ethyl, ethylene, ethylidene, vinyl, ethylidyne, acetylene, vinylidene, ethynyl, and ethynylene (involving regular versions of the species) are visually depicted in Figure 2. The sequence ethane → ethyl → ethylene → vinyl → acetylene → ethynyl → ethynylene is what most chemists would tend to select as the representative path that starts at CH₃CH₃ and strips one hydrogen at the time to arrive at C₂. The C–H BDEs along that sequence are 421.77 ± 0.26 , 150.59 ± 0.27 , 462.46 ± 0.33 , 149.36 ± 0.32 , 557.71 ± 0.08 , $478.69 \pm 0.26 \text{ kJ/mol}$ at 298.15 K. Except for the last step in the sequence, one immediately notices a high value–low value–high value alternation. The general pattern of such alternations has been noted before^{72,117} (and juxtaposed to the similar, but less pronounced pattern found in the analogous Si₂H_n system). As analyzed in more detail during the discussions of the individual species (*vide supra*), the low values are caused by concomitant strengthening of the C–C bond from single to double or from double to triple, the exception being the last member of the series, C₂, where the C–C bond acquires a peculiar strength that is somewhere between a single and a double bond strength. Indeed, the C–C BDEs along the same sequence are 376.66 ± 0.19 , 418.03 ± 0.31 , 730.59 ± 0.24 , 690.72 ± 0.36 , $963.96 \pm$

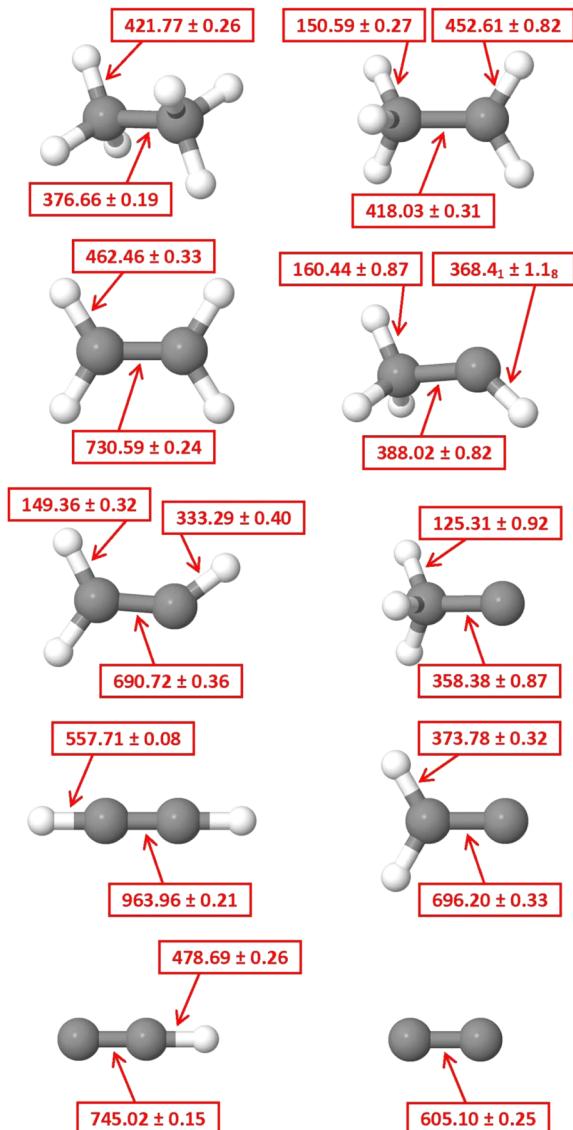


Figure 2. Sequential bond dissociation enthalpies of ethane (in kJ/mol at 298.15 K).

0.21, 745.02 ± 0.15 , 605.10 ± 0.25 kJ/mol at 298.15 K, corresponding to single, single, double, double, triple, double, one-and-a-half. The BDEs depicted in Figure 2 offer several different paths that can lead from ethane to unbound atoms, some of which may need to include the BDEs of CH_n species shown in Figure 1. Of course, whatever the chosen path, as long as the end result is a set of unbound regular atomic species, the BDEs along the path must sum up to the total atomization enthalpy of ethane, $\text{TAE}_{298}(\text{CH}_3\text{CH}_3) = 2825.67 \pm 0.14$ kJ/mol (2787.30 kJ/mol at 0 K).

Of all the carbon–carbon bonds in the C_2H_n system, the bond in C_2 is undeniably the most intriguing. The nature of chemical bonding in ethynylene has been a conundrum for a long time,^{154–158} receiving renewed attention^{159–162} after the recent appearance of a spirited discussion on the topic.^{163–165} Though the underlying idea was explored by Schleyer et al.¹⁵⁵ more than two decades ago, the current controversy was ignited by an interpretation of the VB description of ethynylene by Shaik et al.^{158,166} that led to the claim that the intrinsic bond in

C_2 is quadruple: one σ bond, two π bonds, and one weak “inverted” bond.

Of course, since a quadruple bond ought to be stronger than a triple bond, this immediately creates the expectation that $\text{BDE}(\text{C–C}) > \text{BDE}(\text{HC–CH})$. Ordinary thermodynamics hardly provides support for this, since $\text{BDE}(\text{C–C}) \ll \text{BDE}(\text{HC–CH})$ and, in fact, $\text{BDE}(\text{CH}_3\text{–CH}_3) < \text{BDE}(\text{C–C}) < \text{BDE}(\text{CH}_2\text{–CH}_2)$, as discussed above. The *sine qua non* relation of $\text{BDE}(\text{C–C}) > \text{BDE}(\text{HC–CH})$ can be obtained^{158,163,166} by referring the BDEs to a particular set of dissociation products: ${}^4\text{CH}$, which has three unpaired electrons and was discussed above, and $\text{C}({}^5\text{S}_2)$, which has four unpaired electrons and is higher^{167,168} than the ${}^3\text{P}_0$ ground state of C by $33\,735.22\text{ cm}^{-1}$ (403.563 kJ/mol). Considering excited dissociation products during an analysis of sequential BDEs can be a useful and justified exercise: Noting that the ground state of SiH_2 and GeH_2 is singlet, rather than triplet (which would have the required electrons already uncoupled, as it does in CH_2) explains^{167,169} the striking difference between the sequential bond patterns of CH_4 and SiH_4 or GeH_4 . In acetylene, the choice of ${}^4\text{CH} + {}^4\text{CH}$ as the dissociation asymptote boosts the $\text{C}\equiv\text{C}$ bond by approximately 15% (to $1107.4_8 \pm 1.1_8$ kJ/mol at 298.15 K, 1100.2_6 kJ/mol at 0 K, see Table 2), while in C_2 the choice of $\text{C}({}^5\text{S}_2) + \text{C}({}^5\text{S}_2)$ increases the bond strength by more than a factor of 2 (to 1411.55 ± 0.25 kJ/mol at 298.15 K, 1409.72 kJ/mol at 0 K, vs the current BDE_{298} of 605.10 kJ/mol), making the latter approximately 27% stronger than the (boosted) bond in acetylene, in apparent support of the quadruple bond claim. However, once $\text{C}({}^5\text{S}_2)$ and ${}^4\text{CH}$ are selected as reference species for BDEs of C_2 and HCCH , the same choice needs to be consistently applied to all other affected BDEs in the C_2H_n system, as well as to the CH_n system, which becomes automatically involved in the BDE sequence once a carbon–carbon bond is dissociated. Consistently propagating this particular choice of reference species would, for example, boost the carbon–carbon bond in CH_3C by more than a factor of 2 (to 761.60 ± 0.87 kJ/mol at 298.15 K, 756.17 kJ/mol at 0 K, vs the current BDE_{298} of 358.38 kJ/mol), qualifying it as a double $\text{C}\equiv\text{C}$ bond. It would also increase the vinylidene carbon–carbon bond by 58% (to 1099.43 ± 0.33 kJ/mol at 298.15 K, 1094.64 kJ/mol at 0 K, vs the current BDE_{298} of 696.20 kJ/mol), making it a triple $\text{C}\equiv\text{C}$ bond, only 8.05 kJ/mol shy of the (boosted) bond in acetylene. The carbon–carbon bond in HCC would become stronger by 64% (to 1220.00 ± 0.60 kJ/mol at 298.15 K, 1215.64 kJ/mol at 0 K, vs the current BDE_{298} of 745.02 kJ/mol), or 10% stronger than the (boosted) bond in acetylene. Within the CH_n system, the C–H bond in methylene would receive a moderate 17% boost (to 494.36 ± 0.60 kJ/mol at 298.15 K, 489.62 kJ/mol at 0 K, vs the current BDE_{298} of 422.60 kJ/mol), but the $\text{BDE}(\text{C–H})$ would become outstandingly high (670.23 ± 0.59 kJ/mol at 298.15 K, 666.45 kJ/mol at 0 K, vs the current BDE_{298} of 338.77 kJ/mol), significantly stronger (between 176 and 231 kJ/mol) than any other C–H bond in the CH_n system, and, for that matter, stronger than any C–H bond in the C_2H_n system, including the notoriously strong C–H bond in acetylene (by 112.52 kJ/mol). These consequences have yet to be analyzed and rationalized in terms of VB models that could justify them in terms of bonding contributions.

In contrast to the above, a simple visual inspection of canonical MOs suggests that C_2 , just like acetylene, has two π bonds, but that, unlike acetylene, it appears to be missing a σ bond, a situation sometimes described as “suspended π bonds”.

Given that C_2 is inherently a multireference problem, an interpretation of bonding based on MOs populated in the ground-state determinant is admittedly simplistic. It certainly cannot give a *complete* description of the bonding in C_2 , since the ground-state determinant contributes only about 70% to the wave function. However, 70% is a substantial enough contribution that should at least approximately define the bulk of the bonding pattern, and thus the consequences of a canonical MO picture warrant a closer inspection. As discussed above, in the C_2H_n system the ratio of the prototypical triple $C\equiv C$ in acetylene and single C–C in ethane is not three, but only about 2.56. One is thus tempted to anticipate that a hypothetical C_2 molecule that has two π C–C bonds but is missing a σ C–C bond ought to have a bond strength that is approximately 1.56 times larger than the single BDE₂₉₈(CH₃–CH₃). Curiously enough, this naïve prediction is within hailing distance from the actual ratio of 1.61 found for C_2 (*vide supra*). The quantity [BDE₂₉₈(HC–CH) – BDE₂₉₈(CH₃–CH₃)], which amounts to 587.30 ± 0.28 kJ/mol and roughly estimates the strength of two π C–C bonds in the C_2H_n system, only slightly underestimates (17.80 ± 0.36 kJ/mol) the actual BDE₂₉₈ of ethynylene, suggesting that any additional bonding beyond the suspended π bonds adds very little to the bond strength of C_2 . A recent GVB study of ethynylene by Xu and Dunning¹⁶¹ comes to a very similar conclusion, indicating that out of the four shared electron pairs (two π and two σ), which are the basis for the putative quadruple bond, the two pairs in the σ system spatially overlap, negating their bonding contribution by Pauli repulsion.

ATcT Value for $\Delta_fH^\circ(O)$. The enthalpy of formation of oxygen atom is one of the most fundamental (“key”²²) thermochemical quantities. Oxygen atom is represented in ATcT as three species: regular (^{eq}O or simply O), triplet-only (³O) and singlet-only (¹O). By definition, $\Delta_fH^\circ_0(O) \equiv \Delta_fH^\circ_0(^3O)$. As in several other cases of split-species discussed above, $\Delta_fH^\circ_{298}(^{eq}O) \cong \Delta_fH^\circ_{298}(^3O)$ for all practical purposes. The ATcT enthalpies of formation, truncated to three digits, are $\Delta_fH^\circ_{298}(^{eq}O) = \Delta_fH^\circ_{298}(^3O) = 249.229 \pm 0.002$ kJ/mol (246.844 kJ/mol at 0 K) and $\Delta_fH^\circ_{298}(^1O) = 438.523 \pm 0.002$ kJ/mol (436.666 kJ/mol at 0 K). The ATcT value for O is the same as that given before.^{14,16–19} The corresponding CODATA value²² (249.18 ± 0.10 kJ/mol at 298.15 K) is significantly less accurate, but, within its uncertainty, consistent with the ATcT value. The genesis of the ATcT value was discussed earlier.^{14,19}

ATcT Values for $\Delta_fH^\circ(OH)$ and BDE(OH). Hydroxyl is a very important species both in combustion and in the atmosphere, as well as in many other chemical environments. The enthalpy of formation of hydroxyl relates to the definition of several BDEs in the methanol system that will be discussed below (*vide infra*). The current ATcT value for the enthalpy of formation of hydroxyl is $\Delta_fH^\circ_{298}(OH) = 37.490 \pm 0.026$ kJ/mol (37.250 kJ/mol at 0 K). Except for a barely noticeable difference in the least significant digit, it is identical to the previously published¹⁹ ATcT value (37.492 ± 0.026 kJ/mol at 298.15 K). The ATcT value fully confirms (and further refines) the revision proposed about a decade and a half ago by Ruscic et al.^{170,171} (37.28 ± 0.30 kJ/mol at 298.15 K). The latter utilized a cohort of photoionization measurements and the best available theoretical treatments, significantly revising the values for $\Delta_fH^\circ(OH)$ listed in traditional tables and demonstrating that their basis, which relied on ostensibly unquestionable spectroscopic estimates of $D_0(OH)$, is incorrect.

The provenance of the ATcT value for $\Delta_fH^\circ(OH)$ is quite distributed; it takes 197 determinations to pedigree 90% of the provenance, and 2446 for 99%. The ATcT enthalpy of formation for hydroxyl is highly correlated with that of water ($r_{OH,H_2O} = 0.9991$), and thus it is not particularly surprising that many significant contributors are in common, with the important addition of determinations that help define $D_0(H_2O)$, such as the components of the related positive ion cycle^{170,171} and subsequent direct measurements by Harich et al.,¹⁷² Maksyutenko et al.,¹⁷³ and Boyarkin et al.¹⁷⁴ The high value for the correlation coefficient r_{OH,H_2O} indicates that the uncertainty of the ATcT enthalpy of formation of hydroxyl is nearly entirely inherited from that of water.

The ATcT value for the bond dissociation enthalpy of OH is $BDE_{298}(OH) = 429.737 \pm 0.027$ kJ/mol (425.628 kJ/mol at 0 K). Two additional variants, involving dissociation to triplet-only and singlet-only oxygen atom, are given in Table 3.

ATcT Values for $\Delta_fH^\circ(CH_3OH)$ and BDE(CH₃–OH). The ATcT enthalpy of formation of gas-phase methanol is $\Delta_fH^\circ_{298}(CH_3OH) = -200.71 \pm 0.16$ kJ/mol (-189.83 kJ/mol at 0 K), more accurate than the corresponding 298.15 K values found in Pedley et al.³⁹ (-201.5 ± 0.3 kJ/mol), Gurvich et al.²⁴ (-201.0 ± 0.6 kJ/mol), or the NBS tables^{40,41} (-200.66 ± 0.40 kJ/mol).

The provenance of the ATcT enthalpy of formation of methanol is quite distributed, the top 90% being spread over 168 determinations, with 965 determinations needed to pedigree 99%. The provenance is somewhat top-heavy, with the combustion calorimetry of gas-phase methanol by Rossini^{175–178} emerging as the most prominent contributor (49.4%). Other experimental contributors include the combustion calorimetry of hydrogen^{45,51,52} (2.4%) and of liquid methanol¹⁷⁹ (1.9%), photoionization measurements of AE_0 of CH_2OH^+ from methanol by Borkar et al.¹⁸⁰ (1.6%), the determination of $D_0(CH_2O-H)$ by Ryazanov et al.¹⁸¹ (1.1%), etc. Theoretical determinations also play a considerable role here, such as the 0 K proton affinity of formaldehyde at the FP level of theory by Czakó et al.¹⁸² (10.2%), TAE₀ of methanol at the W4 level by Karton et al.⁷⁹ (1.5%), $D_0(CH_2O-H)$ computed using CCSD(T)/CBS with higher level corrections by Marenich and Boggs¹⁸³ (0.9%), etc.

The ATcT value for the C–O bond dissociation enthalpy in methanol is $BDE_{298}(CH_3-OH) = 384.57 \pm 0.18$ kJ/mol (376.86 kJ/mol at 0 K) and could be taken to represent the prototypical single C–O bond in the COH_n system.

ATcT Values for $\Delta_fH^\circ(CH_2OH)$, BDE(CH₂–OH), and BDE(H–CH₂OH). The ATcT value for the enthalpy of formation of hydroxymethyl is $\Delta_fH^\circ_{298}(CH_2OH) = -16.57 \pm 0.33$ kJ/mol (-10.26 kJ/mol at 0 K), significantly more accurate (and more reliable) than the older value found in Gurvich et al.²⁴ (-20 ± 10 kJ/mol at 298.15 K). The current ATcT value is in excellent agreement with the enthalpy of formation obtained by Ruscic and Berkowitz¹⁸⁴ from photoionization studies (-16.6 ± 0.9 kJ/mol at 298.15 K), and contradicts the frequently quoted value given in the evaluation of Tsang⁵⁷ (-9 ± 4 kJ/mol at 298.15 K), which was obtained from kinetic data. The long-standing discrepancy between spectroscopic and kinetic data for this species was commented on by Berkowitz et al.,⁵⁸ (who selected -17.1 ± 3.8 kJ/mol at 298.15 K) and was subsequently addressed by Johnson and Hudgens¹⁸⁵ (who derived -17.8 ± 1.3 kJ/mol at 298.15 K), all of which was taken into account in the IUPAC-sponsored

evaluation⁵⁶ (where -17.0 ± 0.7 kJ/mol was selected as the recommended 298.15 K value).

The provenance of the ATcT value is fairly distributed and includes 84 determinations in the top 90% and 675 determinations in the top 99% of the provenance. The top two contributors are $\text{IE}_a(\text{CH}_2\text{OH})$ from the photoionization studies of Ruscic and Berkowitz^{186,187} (16.3%) and $D_0(\text{CH}_2\text{O}-\text{H})$ from velocity map imaging studies by Ryazanov et al.¹⁸¹ (13.5%), followed by the theoretical determination of the latter bond dissociation energy by Marenich and Boggs¹⁸³ (10.7%), combustion calorimetry of methanol by Rossini¹⁷⁵ (5.0%), $\text{IE}_a(\text{CH}_2\text{OH})$ from the photoionization studies of Dyke et al.¹⁸⁸ (3.8%), the second law analysis of equilibria obtained from kinetic studies of methanol bromination by Dóbé et al.¹⁸⁹ (3.0%), the theoretical $D_0(\text{CH}_2\text{O}-\text{H})$ obtained by Kamarchik et al.¹⁹⁰ at the ROCCSD(T)/CBS level (2.9%), the theoretical $\text{TAE}_0(\text{CH}_2\text{OH})$ at the FPD level by Matus et al.¹⁹¹ (2.3%), $\text{IE}_a(\text{CH}_2\text{OH})$ from the photoionization studies of Tao et al.¹⁹² (1.8%), the theoretical energy difference between methoxy and hydroxymethyl at the FPD level by Matus et al.¹⁹¹ (1.7%), etc.

The C–O bond dissociation enthalpy of hydroxymethyl is $\text{BDE}_{298}(\text{CH}_2-\text{OH}) = 445.58 \pm 0.34$ kJ/mol (438.47 kJ/mol at 0 K); two more variants involving the dissociation to triplet-only and singlet-only methylene species are given in Table 3. This BDE is significantly higher (by 61.01 ± 0.34 kJ/mol) than the prototypical single C–O BDE in methanol.

The C–H bond dissociation enthalpy of methanol is $\text{BDE}_{298}(\text{H}-\text{CH}_2\text{OH}) = 402.14 \pm 0.32$ kJ/mol (395.60 kJ/mol at 0 K). Using the familiar Maxwell's demon scenario, it can be shown that this BDE would correspond to the BDE of methyl,¹⁹³ and is weaker than the latter by 61.01 ± 0.34 kJ/mol because of the concomitant strengthening of the C–O bond in going from methanol to hydroxymethyl.

ATcT Values for $\Delta_f H^\circ(\text{CH}_3\text{O})$, $\text{BDE}(\text{CH}_3-\text{O})$, and $\text{BDE}(\text{CH}_3\text{O}-\text{H})$. The ATcT value for the enthalpy of formation of methoxy is $\Delta_f H^\circ_{298}(\text{CH}_3\text{O}) = 21.53 \pm 0.34$ kJ/mol (28.90 kJ/mol at 0 K). The recommendation of Berkowitz et al.⁵⁸ (17.2 ± 3.8 kJ/mol at 298.15 K) is considerably lower, and the older value found in Gurvich et al.²⁴ (13 ± 4 kJ/mol at 298.15 K) even more so. The latter two values are in contrast to the recommendation of the IUPAC-sponsored evaluation⁵⁶ (21.0 ± 2.1 kJ/mol at 298.15 K), which is in excellent agreement with the current (and considerably more accurate) ATcT value.

The provenance of the ATcT enthalpy of formation of methoxy is quite distributed, with 170 determinations in the top 90%, and 667 in the top 99%. The primary contributors are the measurement by Ervin and DeTuri^{194,195} of the gas-phase acidity of methanol relative to that of hydrogen fluoride (7.9%), the C–O bond dissociation energy of methoxy by Osborn et al.^{196,197} (7.0%), the combustion calorimetry of methanol by Rossini¹⁷⁵ (3.5%), the C–H bond dissociation energy of methoxy by Dertinger et al.¹⁹⁸ (3.3%), the C–O bond dissociation energy of methoxy and the O–H bond dissociation energy in methanol computed by Marenich and Boggs¹⁸³ at the CCSD(T)/CBS level with additional higher-level corrections (2.8% and 2.2%), $\text{TAE}_0(\text{CH}_3\text{O}^-)$ computed by Matus et al.¹⁹¹ at the FPD level of theory (2.2%), $\text{EA}_a(\text{CH}_3\text{O})$ measured by Nee et al.¹⁹⁹ (2.1%), $\text{TAE}_0(\text{CH}_3\text{O})$ at the FPD level by Feller et al.⁸² (2.0%), the energy difference between the isomeric species CH_3O and CH_2OH computed at the FPD level by Matus et al.¹⁹¹ (1.9%), etc.

The ATcT value for the C–O bond dissociation enthalpy in methoxy is $\text{BDE}_{298}(\text{CH}_3-\text{O}) = 374.07 \pm 0.35$ kJ/mol (367.73

kJ/mol at 0 K), with two more variants involving the dissociation to triplet-only and singlet-only O atom listed in Table 3. The C–O bond in methoxy is marginally weaker (by 10.50 ± 0.34 kJ/mol at 298.15 K) than the prototypical C–O bond in methanol.

The ATcT value for the O–H bond dissociation enthalpy in methanol is $\text{BDE}_{298}(\text{CH}_3\text{O}-\text{H}) = 440.24 \pm 0.34$ kJ/mol (434.76 kJ/mol at 0 K). In the Maxwell's demon two-phase scenario, this BDE would correspond to the BDE of hydroxyl.²⁰⁰ It is, in fact, slightly stronger than the latter (by 10.50 ± 0.34 kJ/mol at 298.15 K), the gain corresponding to the concomitant weakening of the C–O bond in going from methanol to methoxy.

ATcT Values for $\Delta_f H^\circ(\text{CH}_2\text{O})$, $\text{BDE}(\text{CH}_2-\text{O})$, $\text{BDE}(\text{H}-\text{CH}_2\text{O})$, and $\text{BDE}(\text{CH}_2\text{O}-\text{H})$. The ATcT value for the enthalpy of formation of gas-phase formaldehyde is $\Delta_f H^\circ_{298}(\text{CH}_2\text{O}) = -109.19 \pm 0.10$ kJ/mol (-105.35 kJ/mol at 0 K). The values found in standard compilations, such as Pedley et al.³⁹ (-108.6 ± 0.5 kJ/mol at 298.15 K), Gurvich et al.²⁴ (-108.7 ± 0.5 kJ/mol at 298.15 K), and the NBS tables^{40,41} (-108.57 ± 0.40 kJ/mol at 298.15 K), are less accurate and slightly on the high (less negative) side, with the exception of the value found in the JANAF tables²³ (-115.9 ± 6.3 kJ/mol at 298.15 K), which is even less accurate and noticeably more negative.

The provenance of the ATcT enthalpy of formation of formaldehyde is quite distributed, requiring 152 determinations to pedigree 90% and 1349 to pedigree 99% of the provenance. There are 10 contributors with individual contributions of 2% or more, only one of which is of experimental origin: the combustion calorimetry of gas-phase formaldehyde by Fletcher and Pilcher²⁰¹ (2.1%). The other nine top contributors are derived from state-of-the-art theory: the 0 K absolute proton affinity of CO, the relative proton affinity of CO vs NH_3 , and the absolute proton affinity of NH_3 , obtained at the FP level of theory (using up to CCSDTQ) by Czakó et al.²⁰² (22.5, 3.0, and 2.1%, respectively), the 0 K enthalpy of hydrogenation of CO and the absolute proton affinity of formaldehyde obtained at the FP level by Czakó et al.¹⁸² (11.5 and 2.9%), the 0 K enthalpy of the isodesmic reaction $2 \text{CH}_2\text{O} \rightarrow \text{CH}_4 + \text{CO}_2$ recovered from W4.2, W4, and W4L results of Karton et al.⁷⁶ (3.4, 3.4, and 2.3%), and the HEAT 345-QP TAE_0 of formyl by Harding et al.⁵⁴ (2.6%).

The ATcT bond dissociation enthalpy of the C=O bond in formaldehyde is $\text{BDE}_{298}(\text{CH}_2-\text{O}) = 749.93 \pm 0.15$ kJ/mol (743.15 kJ/mol at 0 K); four additional variants corresponding to dissociation asymptotes involving nonstandard methylene and oxygen atom species are listed in Table 3. The ratio $\text{BDE}_{298}(\text{CH}_2-\text{O})/\text{BDE}_{298}(\text{CH}_3-\text{OH})$ is 1.9500 ± 0.0010 , clearly suggesting a double bond, and thus $\text{BDE}(\text{CH}_2-\text{O})$ can be taken to represent the prototypical C=O bond in the COH_n system.

The C–H BDE of methoxy is $\text{BDE}_{298}(\text{H}-\text{CH}_2\text{O}) = 87.28 \pm 0.35$ kJ/mol (81.78 kJ/mol at 0 K). The striking weakness of this bond is caused by the concomitant change in the carbon–oxygen bonding from a single C–O bond in methoxy to a double C=O bond in formaldehyde (gaining stability by 375.86 ± 0.37 kJ/mol at 298.15 K). In the Maxwell's demon scenario, the removal of hydrogen, while keeping the C–O bond frozen, would cost 463.14 kJ/mol in enthalpy at 298.15 K, exactly as much as the C–H BDE in methyl.²⁰³

The O–H BDE in hydroxymethyl is $\text{BDE}_{298}(\text{CH}_2\text{O}-\text{H}) = 125.38 \pm 0.33$ kJ/mol (120.94 kJ/mol at 0 K). As above, the unusual weakness of this bond is caused by the concomitant

strengthening in the carbon–oxygen bonding from a single C–O bond in hydroxymethyl to a double C=O bond in formaldehyde (increasing in stability by 304.35 ± 0.33 kJ/mol at 298.15 K). In the Maxwell's demon scenario, the first step would cost 429.73 kJ/mol in enthalpy, exactly as much as the O–H BDE in hydroxyl.²⁰⁴

ATcT Values for $\Delta_f H^\circ(\text{HCOH})$, $\text{BDE}(\text{HC-OH})$, and $\text{BDE}(\text{H-CHOH})$. Hydroxymethylene is the less stable isomer of formaldehyde. Though it has been postulated to exist for a long time, it was observed only recently,^{205–207} by trapping it in an argon matrix at 11 K. The singlet ground state has two conformers, *trans* and *cis*, with the former being more stable. The excited triplet state is *gauche*. Hydroxymethylene is represented in ATcT as four species: regular hydroxymethylene (^{eq}HCOH or just HCOH), which is assumed to be equilibrated over the *cis* and *trans* singlets and the *gauche* triplet state, and the following nonstandard species: *trans*-only singlet hydroxymethylene (*t*¹HCOH), *cis*-only singlet hydroxymethylene (*c*¹HCOH), and *gauche* triplet-only hydroxymethylene (³HCOH). The corresponding ATcT enthalpies of formation are $\Delta_f H^\circ_{298}(\text{HCOH}) = 108.64 \pm 0.33$ kJ/mol (112.40 kJ/mol at 0 K), $\Delta_f H^\circ_{298}(\text{i}^1\text{HCOH}) = 108.63 \pm 0.33$ kJ/mol (112.40 kJ/mol at 0 K), $\Delta_f H^\circ_{298}(\text{c}^1\text{HCOH}) = 127.11 \pm 0.34$ kJ/mol (130.86 kJ/mol at 0 K), and $\Delta_f H^\circ_{298}(\text{g}^3\text{HCOH}) = 216.0_6 \pm 1.1_0$ kJ/mol (219.0₁ kJ/mol at 0 K). Standard thermochemical tabulations do not provide information on this species.

The provenance of the ATcT enthalpy of formation of hydroxymethylene is fairly distributed: 52 determinations account for the top 90%, and 249 determinations for 99% of the provenance. Not surprisingly, all relevant contributors are from theory. There are 15, fairly evenly distributed, contributors with individual contributions of 2% or more. The 0 K energy difference between *trans*-hydroxymethylene and formaldehyde obtained by Schreiner et al.²⁰⁵ at the FP level of theory (11.1%), the same quantity as computed at the W4 level of theory by Karton et al.⁷⁹ (8.4%), and the TAE₀(*t*-HCOH) obtained by Feller et al.²⁰⁸ (6.5%), emerge as the top three contributors. Other important contributors include the 0 K energy difference between *cis*-hydroxymethylene and formaldehyde, between *trans*- and *cis*-hydroxymethylene, and the 0 K enthalpy of hydrogenation of CO, all obtained at the FP level of theory,²⁰⁵ and similar determinations involving energy differences between *trans*-hydroxymethylene, *cis*-hydroxymethylene, and formaldehyde, as well as TAE₀(*c*-HCOH), obtained at the W4 level of theory by Karton et al.⁷⁹

The ATcT value for the C–O BDE in hydroxymethylene is $\text{BDE}_{298}(\text{HC-OH}) = 524.97 \pm 0.34$ kJ/mol (517.63 kJ/mol at 0 K), using regular hydroxymethylene and regular methylidyne species. Eleven additional variants, iterating through various combinations of nonstandard hydroxymethylene and methylidyne are given in Table 3. The C–O bond in hydroxymethylene is significantly stronger than the single C–O bond in methanol (by 140.40 ± 0.37 kJ/mol at 298.15 K), but considerably weaker (by 224.96 ± 0.35 kJ/mol at 298.15 K) than the C=O bond in formaldehyde.

The ATcT value for the C–H BDE in hydroxymethyl is $\text{BDE}_{298}(\text{H-CHOH}) = 343.21 \pm 0.45$ kJ/mol (338.69 kJ/mol at 0 K) to produce regular hydroxymethylene, with other variants corresponding to nonstandard hydroxymethylene species given in Table 3. This BDE is weaker (by 79.39 ± 0.47 kJ/mol at 298.15 K) than $\text{BDE}_{298}(\text{H-CH})$, to which it should be compared,²⁰⁹ the difference being directly attribut-

able to the concomitant strengthening of the C–O bond in going from hydroxymethyl to hydroxymethylene.

ATcT Values for $\Delta_f H^\circ(\text{HCO})$, $\text{BDE}(\text{HC-O})$, $\text{BDE}(\text{H-CHO})$, and $\text{BDE}(\text{HCO-H})$. The ATcT enthalpy of formation of formyl is $\Delta_f H^\circ_{298}(\text{HCO}) = 41.80 \pm 0.10$ kJ/mol (41.43 kJ/mol at 0 K), significantly more accurate than the 298.15 K values listed in conventional tabulations, such as JANAF²³ (43.5 ± 8.0 kJ/mol), Gurvich et al.²⁴ (42 ± 5 kJ/mol), and the NBS tables^{40,41} (43.1 ± 4.0 kJ/mol), or in the evaluation by Berkowitz et al.⁵⁸ (41.7 ± 0.8 kJ/mol), which relied on $D_0(\text{H-CHO})$ determined by Chuang et al.²¹⁰

The provenance of the ATcT enthalpy of formation of formyl is very distributed. It takes 152 determinations to pedigree 90%, and 1348 determinations to pedigree 99% of the provenance. There are 10 determinations with individual contributions of 2% or more. The ATcT enthalpy of formation of formyl is highly correlated to that of formaldehyde ($r_{\text{HCO},\text{H}_2\text{CO}} = 0.99819$), so it is not surprising that the top contributors are nearly the same in both cases. However, if one uses variance decomposition to look at the *difference* in the provenances of these two ATcT enthalpies of formation, one contributor immediately takes the lead: the very accurate experimental bond dissociation energy of formaldehyde measured by Terentis and Kable.²¹¹

The ATcT value for the C–O bond dissociation enthalpy of formyl is $\text{BDE}_{298}(\text{HC-O}) = 803.54 \pm 0.14$ kJ/mol (798.20 kJ/mol at 0 K); four additional variants involving nonstandard methylidyne and nonstandard oxygen atom species are given in Table 3. This bond is noticeably stronger (by 53.61 ± 0.12 kJ/mol at 298.15 K) than the double C=O bond in formaldehyde.

The C–H bond dissociation enthalpy in formaldehyde is $\text{BDE}_{298}(\text{H-CHO}) = 368.988 \pm 0.006$ kJ/mol (362.810 kJ/mol at 0 K). In the Maxwell's demon scenario, this BDE corresponds exactly to the BDE of methylene,²¹² the lowering of its strength being directly attributable to the concomitant increase in strength of the carbon–carbon bond (by 53.61 ± 0.12 kJ/mol) in going from formaldehyde to formyl.

The O–H bond dissociation enthalpy in regular hydroxymethylene is $\text{BDE}_{298}(\text{HCO-H}) = 151.16 \pm 0.32$ kJ/mol (145.06 kJ/mol at 0 K); analogous BDEs involving nonstandard hydroxymethylene are given in Table 3. This bond is significantly weaker than the O–H bond in methanol (by 289.08 ± 0.46 kJ/mol at 298.15 K), though it is modestly stronger (by 25.78 ± 0.45 kJ/mol at 298.15 K) than the O–H bond in hydroxymethyl. As in the latter case, the weakness is entirely attributable to the concomitant increase of the carbon–oxygen bond strength in going from hydroxymethylene to formyl (by 278.57 ± 0.32 kJ/mol at 298.15 K). In the Maxwell's scenario, this BDE would be directly comparable²¹³ to $\text{BDE}(\text{OH})$.

ATcT Values for $\Delta_f H^\circ(\text{COH})$, $\text{BDE}(\text{C-OH})$, and $\text{BDE}(\text{H-COH})$. Isoformyl is the less stable isomer of formyl. Its ATcT enthalpy of formation is $\Delta_f H^\circ_{298}(\text{COH}) = 217.69 \pm 0.67$ kJ/mol (217.31 kJ/mol at 0 K). Standard thermochemical compilations do not list this species.

The provenance of the ATcT enthalpy of formation is rather modestly distributed. The top 90% of the provenance contains 24 determinations, the top 99% contains 73 determinations, all of which come from theory with the exception of two: the combustion calorimetry of formaldehyde²⁰¹ and the electron affinity of HCO.²¹⁴ The distribution is top-heavy: The primary contributor is the 0 K energy difference between isoformyl and

formyl, computed at the CCSD(T)/CBS level, including higher-level corrections, by Marenich and Boggs²¹⁵ (66.0%). The next 13 contributors cumulatively contribute 16.5%, ranging individually between 2.3% and 1.0%, and include IE_a(COH), the 0 K energy difference between HCO and COH, and D_0 (CO–H), all obtained in-house at the W1, G4, and CBS-APNO composite levels of theory.

The current ATcT value for the carbon–oxygen bond dissociation enthalpy of isoformyl is $BDE_{298}(C-OH) = 536.69 \pm 0.67$ kJ/mol (531.35 kJ/mol at 0 K), with two additional variants corresponding to dissociation to triplet-only and singlet-only C atom species given in Table 3. This bond is significantly weaker than the C=O bond in formaldehyde (by 213.24 ± 0.67 kJ/mol at 298.15 K), and even more so than C=O bond in formyl (by 266.85 ± 0.67 kJ/mol at 298.15 K), but considerably stronger than the single C–O bond in methanol (by 152.12 ± 0.69 kJ/mol at 298.15 K). The carbon–oxygen bond in isoformyl is, in fact, quite comparable (stronger only by 11.72 ± 0.74 kJ/mol at 298.15 K) to the carbon–oxygen bond in regular hydroxymethylene.

The C–H bond dissociation enthalpy in hydroxymethylene is $BDE_{298}(H-COH) = 327.04 \pm 0.73$ kJ/mol (320.94 kJ/mol at 0 K). Additional variants of this BDE, involving nonstandard versions of hydroxymethylene are listed in Table 3. In the Maxwell's demon scenario, this bond would correspond to the bond in methylidyne,²¹⁶ from which it is marginally weaker (by 11.72 ± 0.74 kJ/mol at 298.15 K) on account of the modest strengthening of the carbon–oxygen bond in going from hydroxymethylene to isoformyl.

ATcT Values for $\Delta H^\circ(CO)$, $BDE(CO)$, $BDE(H-CO)$, and $BDE(CO-H)$. As discussed earlier, the enthalpy of formation of carbon monoxide is intimately related to the determination of the enthalpy of formation of C atom. The ATcT value is $\Delta H^\circ_{298}(CO) = -110.523 \pm 0.026$ kJ/mol (-113.803 kJ/mol at 0 K), significantly more accurate than the corresponding CODATA value (-110.53 ± 0.17 kJ/mol at 298.15 K). The current value is essentially identical to the previously¹⁹ given ATcT value (-110.522 ± 0.026 kJ/mol at 298.15 K).

The ATcT value for the BDE of carbon monoxide is $BDE_{298}(CO) = 1076.638 \pm 0.051$ kJ/mol (1072.047 kJ/mol at 0 K), with additional variants involving various combinations of nonstandard C and O atom species listed in Table 3. Carbon monoxide is the second most abundant molecule in the universe. It has a spectacularly strong bond: Its dative triple bond is the strongest chemical bond known. The ratio $BDE_{298}(CO)/BDE_{298}(CH_3-OH)$ is 2.7996 ± 0.0013 , similar to (though very slightly larger than) the ratio of the triple and single carbon–carbon bond strengths in the C_2H_n system (*vide supra*). CO is exceptionally stable to thermal dissociation, to the point that this molecule survives in the upper layers of carbon-rich stars, holding the promise that ultra-accurate measurements of its emission from distant objects in the universe can be used as a probe of temporal variation of fundamental constants.^{217,218}

The ATcT value for the C–H BDE of formyl is $BDE_{298}(H-CO) = 65.67 \pm 0.10$ kJ/mol (60.81 kJ/mol at 0 K). This is a remarkably weak C–H bond; the essential reason resides in the concomitant strengthening of the carbon–oxygen bond to form the triply bonded carbon monoxide. In the Maxwell's demon scenario, the phase of relaxing the frozen carbon–oxygen bond would return 273.10 ± 0.14 kJ/mol in enthalpy at 298.15 K, and thus the expenditure during the removal of the hydrogen atom with the frozen carbon–oxygen bond would be 338.77

kJ/mol at 298.15 K, which exactly corresponds²¹⁹ to $BDE_{298}(CH)$.

The ATcT value for the O–H BDE in isoformyl is $BDE_{298}(CO-H) = -110.21 \pm 0.67$ kJ/mol (-115.07 kJ/mol at 0 K), indicating that isoformyl is less stable than the CO + H dissociation asymptote. The essential weakness of this bond—to the point of becoming an exothermic dissociation—is again attributable to the concomitant strengthening of the carbon–oxygen bond to form the triple bond in CO. In the Maxwell's demon scenario, the second phase, corresponding to the carbon–oxygen bond relaxation, would return a whopping 539.95 ± 0.67 kJ/mol at 298.15 K, while the first phase would cost 429.74 kJ/mol in enthalpy at 298.15 K, exactly²²⁰ as much as $BDE_{298}(OH)$.

Summary of the Sequential BDEs in the COH_n System.

The 298.15 K values for all possible C–H, O–H, and C–O BDEs of methanol, hydroxymethyl, methoxy, formaldehyde, hydroxymethylene, formyl, isoformyl, and carbon monoxide, involving regular versions of chemical species, are visually summarized in Figure 3. In going through the sequential

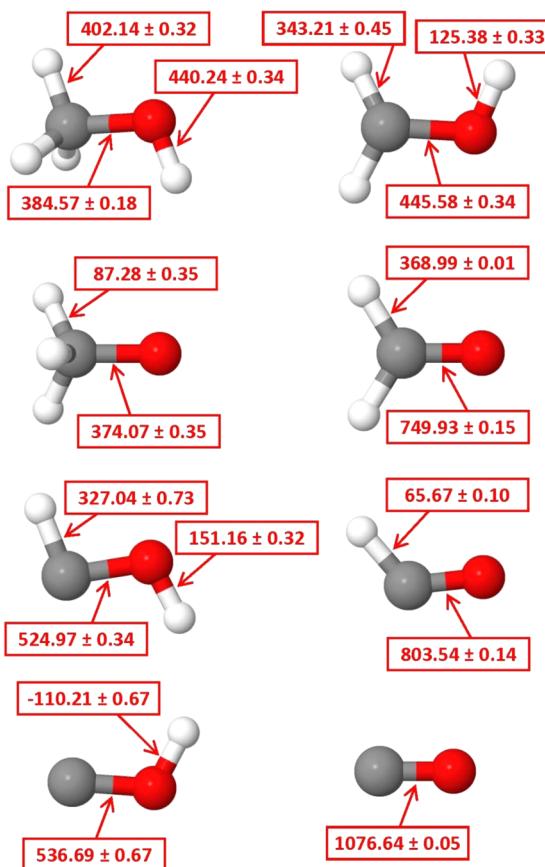


Figure 3. Sequential bond dissociation enthalpies of methanol (in kJ/mol at 298.15 K).

dissociations that lead from methanol to disjoint atoms, several different paths are possible. Irrespective of the path, the sequential BDEs must sum up to the total atomization enthalpy of methanol, $TAE_{298}(CH_3OH) = 2038.82 \pm 0.17$ kJ/mol (2012.21 kJ/mol at 0 K), as long as the final products are unbound atoms in their regular states. Many paths of successive removals of hydrogen atoms, such as methanol → methoxy → formaldehyde → formyl → carbon monoxide, involve pronounced alternations in the bond strengths, similar to the

successive hydrogen removals from ethane. As discussed above, these alternations are directly related to successive strengthening in the carbon–oxygen bond, from single to double, and from double to triple. The strongest C–H bond in the COH_n system is found in methanol, while methoxy and formyl display the weakest C–H bonds. The strongest O–H bond in the COH_n system is also found in methanol, where it is stronger than the C–H bond. However, in all other COH_n species the O–H is markedly weak, significantly weaker than the corresponding C–H bond.

ATcT Values for $\Delta_f H^\circ(\text{H}_2\text{O})$ and BDE(H–OH). While obviously not directly related to the sequential bond dissociations of methanol, water is the final product in the combustion of hydrogen-containing fuels, and is included here for the sake of completeness. The ATcT enthalpy of formation of gas-phase water is $\Delta_f H^\circ_{298}(\text{H}_2\text{O}) = -241.834 \pm 0.026 \text{ kJ/mol}$ (-238.930 kJ/mol at 0 K), which can be compared to the very similar, but slightly less accurate 298.15 K values found in the CODATA compilation²² ($-241.826 \pm 0.040 \text{ kJ/mol}$ at 298.15 K) and in the NBS tables^{40,41} ($-241.818 \pm 0.040 \text{ kJ/mol}$). The current value is nearly identical to the recently published^{18,19} ATcT value ($-241.831 \pm 0.026 \text{ kJ/mol}$), as well as to the initial ATcT value¹⁴ obtained from a much smaller TN ($-241.818 \pm 0.033 \text{ kJ/mol}$).

The genesis of the ATcT value for $\Delta_f H^\circ(\text{H}_2\text{O})$ has been discussed earlier¹⁴ in terms of principal determinations included in the TN. The provenance of $\Delta_f H^\circ(\text{H}_2\text{O})$ is quite distributed, very much like that of $\Delta_f H^\circ(\text{OH})$; it takes 196 determinations to pedigree 90% of the provenance, and 2447 for 99%.

The ATcT value for the bond dissociation enthalpy of water is $\text{BDE}_{298}(\text{H–OH}) = 497.321 \pm 0.002 \text{ kJ/mol}$ (492.215 kJ/mol at 0 K). The BDE of water is substantially stronger (by $57.08 \pm 0.34 \text{ kJ/mol}$ at 298.15 K) than the O–H BDE in methanol. For that matter, $\text{BDE}_{298}(\text{H–OH})$ is stronger than any other O–H or C–H BDE₂₉₈ in the COH_n system, implying that hydrogen abstraction by OH radicals from any species in this system is exothermic at 298.15 K; the same is true for all species in the CH_n and C_2H_n system, with only one exception: acetylene.

ATcT Values for $\Delta_f H^\circ(\text{CO}_2)$ and BDE(O–CO). While carbon dioxide is also not directly involved in the sequential BDEs of methane, ethane, or methanol, it is, like water, one of the final products of the combustion process, and is given here in the interest of completeness. The ATcT enthalpy of formation for carbon dioxide is $\Delta_f H^\circ_{298}(\text{CO}_2) = -393.475 \pm 0.014 \text{ kJ/mol}$ (-393.109 kJ/mol at 0 K), significantly more accurate than the 298.15 K CODATA value ($-393.51 \pm 0.13 \text{ kJ/mol}$). The current value is essentially identical to the recently published^{18,19} ATcT value ($-393.474 \pm 0.014 \text{ kJ/mol}$), as well as to the earlier ATcT value¹⁴ obtained from a much smaller TN ($-393.473 \pm 0.014 \text{ kJ/mol}$). The genesis of the ATcT enthalpy of formation of carbon dioxide has been discussed before.¹⁴

The ATcT BDE of carbon dioxide is $\text{BDE}_{298}(\text{O–CO}) = 532.181 \pm 0.025 \text{ kJ/mol}$ (526.150 kJ/mol at 0 K). Two more variants of this BDE, corresponding to dissociation asymptotes with triplet-only and singlet-only oxygen atom species, are given in Table 3. $\text{BDE}_{298}(\text{O–CO})$ is significantly smaller (by $217.75 \pm 0.15 \text{ kJ/mol}$ at 298.15 K) than the C=O BDE in formaldehyde. As already seen in a number of examples that were discussed above, this BDE appears smaller than one would expect for a double C=O bond because of the concomitant strengthening of the remaining carbon–oxygen bond, to form the tightly bound carbon monoxide molecule.

Summary of the Sequential BDEs in H_2O and CO_2 . The short sequences of successive BDEs of H_2O and CO_2 are visually summarized in Figure 4. In water, the first bond is

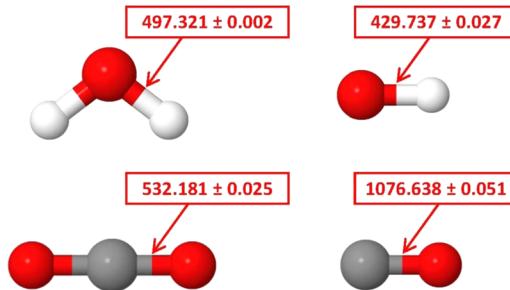


Figure 4. Sequential bond dissociation enthalpies of water and carbon dioxide (in kJ/mol at 298.15 K).

significantly stronger (by $67.584 \pm 0.026 \text{ kJ/mol}$ at 298.15 K) than the second one. Together, these two BDEs sum up to the total atomization enthalpy of water, $\text{TAE}_{298}(\text{H}_2\text{O}) = 927.058 \pm 0.026 \text{ kJ/mol}$ (917.842 kJ/mol at 0 K).

The average O–H bond enthalpy can be obtained from the total atomization enthalpy, and amounts to $\text{BE}_{av,298}(\text{O–H}) = 463.529 \pm 0.013 \text{ kJ/mol}$, somewhat different than the value (461 kJ/mol) given originally by Pauling.⁵ However, in the scheme of average bond enthalpies, this BE_{av} is unlikely to serve as a good representation of O–H bonds in alcohols, or, for that matter, in most other organic compounds, except, perhaps, carboxylic acids.

In CO_2 , the second sequential BDE is dramatically larger than the first (by a rather spectacular $544.457 \pm 0.064 \text{ kJ/mol}$ at 298.15 K). The two sequential bonds sum up to the total atomization enthalpy of carbon dioxide, which is $\text{TAE}_{298}(\text{CO}_2) = 1608.819 \pm 0.049 \text{ kJ/mol}$ (1598.197 kJ/mol at 0 K).

The average C=O bond enthalpy in carbon dioxide, as obtained from its TAE, amounts to $\text{BE}_{av,298}(\text{C=O}) = 804.410 \pm 0.025 \text{ kJ/mol}$. One would have expected that this BE_{av} will provide a reasonable benchmark for the strength of a C=O bond. However, $\text{BE}_{av,298}(\text{C=O})$ obtained from CO_2 is significantly larger (by $54.48 \pm 0.15 \text{ kJ/mol}$) than BDE_{298} for the C=O bond in formaldehyde, which we have selected as the prototypical double C=O bond for the purpose of discussing the sequential BDEs in the COH_n system. As in the case of $\text{BE}_{av}(\text{O–H})$ derived from $\text{TAE}(\text{H}_2\text{O})$, the $\text{BE}_{av}(\text{C=O})$ derived from $\text{TAE}(\text{CO}_2)$ is unlikely to serve as a good representation of C=O bond strengths in organic compounds.

CONCLUSIONS

ATcT thermochemistry for the sequential bond dissociations of methane, ethane, and methanol systems were obtained by solving a large TN (ver. 1.122), which spans over 1180 species and encompasses more than 19 000 determinations. The enthalpies of formation for all related CH_n , C_2H_n , COH_n , CO_n , and H_nO species, at both 298.15 and 0 K, were presented. Their provenances, which are quite distributed and involve a large number of relevant determinations, were analyzed by variance decomposition and discussed in terms of principal contributors. All possible bond dissociation enthalpies, BDE_{298} , and bond dissociation energies, D_0 , in the targeted systems were presented and individually discussed. As hydrogen atoms are successively stripped down, one encounters quite dramatic alternations between high and low values of the enthalpy

needed to remove the next hydrogen atom. These variations can be quantitatively rationalized by the concomitant changes in the strength of the skeletal carbon–carbon or carbon–oxygen bond. In particular, as the skeleton bond changes its character from single to double or from double to triple bond, the gain in the strength of the skeleton bond lowers quite dramatically the enthalpy for the corresponding hydrogen removal. The present ATcT results for the BDEs and for the related enthalpies of formation are the most accurate thermochemical values currently available for these systems.

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Notes

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- (1) The adjective “standard” refers formally to a reference pressure of 1 bar (though for ideal gas species the selected pressure—as long as it is constant—does not actually affect the enthalpy); the temperature T at which BDE is quoted can be chosen arbitrarily (most commonly either 0 or 298.15 K) but needs to be explicitly stated since, like all thermochemistry, BDEs are temperature dependent.
- (2) The exception are bond ruptures in which the dissociating chemical species does not produce two fragments, such as, for example, a ring-opening.
- (3) The “lowest *actually existing* rovibrational level” stipulation implies that additional care needs to be taken when using literature values of D_0 for thermodynamic purposes, since D_0 in spectroscopic work sometimes refers to a hypothetical rotational level that is wiped out by nuclear spin statistics in the dominant isotopologue; see, for example, discussion on O₂ in ref 19. Incidentally, in order to avoid an additional systematic error, theoretical predictions at the highest level of accuracy need to include applicable corrections for rotational zero point energy, on top of the usual corrections for vibrational zero point energy and spin-orbit effects (including additional complexities that occur when the spin-orbit terms are coupled to the rotational angular momentum); see, for example, the discussion of OH in refs 54 and 170, or the discussion of H₃⁺ in the following: Widicus Weaver, S. L.; Woon, D. E.; Ruscic, B.; McCall, B. J. Is HO₂⁺ a Detectable Interstellar Molecule? *Astrophys. J.* **2009**, *697*, 601–609.
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- (21) In rare cases the relevant measurement does, in fact, correspond to a direct determination of an enthalpy of formation or Gibbs energy of formation; examples would be combustion calorimetry of graphite in oxygen to form carbon dioxide or of hydrogen in oxygen to form liquid water, high-temperature equilibrium constant between methane, hydrogen, and graphite, etc.
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(220) BDE(CO–H) corresponds to the enthalpy change in COH → CO + H, BDE(C–OH) to COH → C + OH, BDE(CO) to CO → C + O, and thus the net for BDE(CO–H) + [BDE(CO)) – BDE(C–OH)] corresponds to OH → O + H.