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Introduction to Active Thermochemical Tables: Several "Key" Enthalpies of Formation Revisited[†]

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The concept behind active thermochemical tables (ATcT) is presented. As opposed to traditional sequential thermochemistry, ATcT provides reliable, accurate, and internally consistent thermochemistry by utilizing the thermochemical network (TN) approach. This involves, inter alia, a statistical analysis of thermochemically relevant determinations that define the TN, made possible by redundancies in the TN, such as competing measurements and alternate network pathways that interrelate the various chemical species. The statistical analysis produces a self-consistent TN, from which the optimal thermochemical values are obtained by simultaneous solution in error-weighted space, thus allowing optimal use of all of the knowledge present in the TN. ATcT offers a number of additional features that are not present nor possible in the traditional approach. With ATcT, new knowledge can be painlessly propagated through all affected thermochemical values. ATcT also allows hypothesis testing and evaluation, as well as discovery of weak links in the TN. The latter provides pointers to new experimental or theoretical determinations that will most efficiently improve the underlying thermochemical body of knowledge. The ATcT approach is illustrated by providing improved thermochemistry for several key thermochemical species.

1. Introduction

Knowledge of thermochemical stability of various chemical species is central to almost all aspects of chemistry and essential in many industries. While reasonably accurate thermochemical information is highly desirable in many branches of chemistry, the availability of accurate, reliable, and internally consistent thermochemical values for a broad range of chemical species is a conditio sine qua non in a number of areas of physical chemistry, such as chemical kinetics, construction of reaction mechanisms, formulation of descriptive chemical models that have predictive abilities, etc. Also, the availability of accurate and reliable thermochemistry has been historically the strongest spiritus movens for the development of increasingly sophisticated electronic structure theories, where accurate thermochemical values have served (and are still serving) either as benchmarks for evaluating new theoretical methods or as empirical correctors for adjusting calculated potential energy surfaces. The availability of well-defined and properly quantified uncertainties for principal thermochemical properties, such as enthalpies of formation, that properly convey the inherent degree of confidence that may be placed in these values, is an often neglected (and hence generally underutilized) but equally important aspect that significantly contributes to the overall reliability and consistency of the body of thermochemical knowledge. Given the constantly increasing fidelity of electronic structure calculations, "benchmark" thermochemical values may become misleading or even useless unless they are accompanied by properly quantified uncertainties. In addition, the availability of uncertainties (and their, currently generally absent, full propagation within computer models) will become increasingly important as a tool for estimating the underlying fidelity levels of chemical models and simulations of complex chemical environments, such as flames or the atmosphere. Finally, the availability of a body of reliable and accurate thermochemistry is often a stimulating environment fostering abstraction of generalities that may open new insights into the details of chemical bonding in molecules.

This is the first in a string of planned papers that will report new and improved thermochemical values obtained via active thermochemical tables (ATcT). ATcT is a novel scientific application, centered on a distinctively different paradigm of how to derive accurate, reliable, and internally consistent thermochemical values.

The purpose of this paper is to introduce ATcT, briefly outline the underlying method, and illustrate its capabilities by providing new thermochemistry for a few simple "key" chemical species, which stand at the very foundation of thermochemistry. Subsequent papers in this series will then gradually expose the improved thermochemistry of other species, which will be conveniently aggregated in groups that are related by a common discussion thread.

2. Traditional Sequential Thermochemistry

Thermochemical tables are tabulations of thermochemical properties conveniently sorted by chemical species. Their quality ranges from fully documented critical data evaluations,[1−3] through compilations containing references but not elaborating the reasons for favoring a particular value,[4−7] or lists providing fully referenced multiple values without attempting an evalu-

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ation,[8] to tabulations that select values from other compilations,[9] often ignoring the need to provide detailed referencing. The central thermochemical quantity is usually the enthalpy of formation, and is often accompanied by the Gibbs energy of formation, heat capacity, entropy, enthalpy increment (aka integrated heat capacity), etc. These are most frequently given at the reference temperature of 298.15 K, sometimes also at 0 K, whereas some tables include a wider selection of temperatures. Several compilations specialize in presenting the thermochemistry in the form of polynomials rather than tables.[10,11]

The listed thermochemical properties for a chemical species are derived from more basic determinations, which, for the purpose of the present discussion, may be categorized as generally falling into two categories: determinations that relate to some property of only one species, and that do not depend in any direct way on properties of other species, which we will term species-specific information, and determinations that relate to some property relative to one or more other species, which we will term species-interrelating information. Certain thermochemical quantities (namely, those that are related to the partition function, such as heat capacity, entropy, and enthalpy increment) can be, at least in principle, derived directly from species-specific information, consisting, for example, of spectroscopic measurements (or electronic-structure computations) of the electronic states and their rovibronic levels for gas-phase species or of direct measurements of selected properties (e.g., heat capacity) for condensed-phase species. However, to determine the enthalpy of formation or the Gibbs energy of formation and place it on a common scale, where the origin (zero) is by convention relative to chemical elements in their standard states, the pivoting information has to come from determinations (measurements or computations) that express either the enthalpy of formation or the Gibbs energy of formation relative to other chemical species. With the exception of elements in their reference states, the enthalpy of formation and the Gibbs energy of formation (as well as several others that can be derived from them) cannot be, even in principle, determined without recourse to species-interrelating determinations, such as bond dissociation energies, enthalpies of chemical reactions, kinetic equilibria, electrode potentials, solubility data, etc. (Please note the fine point that two different aggregate states, such as gas-phase and condensed-phase, of the same chemical entity belong, from the thermochemical viewpoint, to two distinct chemical species, each having a different set of temperature-dependent properties.)

The inexorable species-interrelating data leads to intricacies, which are traditionally solved via a sequential approach. The essence of the sequential approach is to disentangle the intricacies of the cross-relationships via a stepwise process. During each step, a new chemical species is adopted and available scientific information is scrutinized. The "best" species-interrelating measurement(s) are selected through a critical evaluation process and then used to obtain, at one temperature, either the enthalpy of formation or the Gibbs energy of formation for that species. One clear limitation is that the approach can utilize only those species-interconnecting determinations that link the currently evaluated species exclusively to species that have been already compiled during previous steps. In practice, the selection of the "best" determinations defines which actual step will be used to arrive at a particular species, and which alternative steps will be ignored or taken only as a secondary check. Once the enthalpy or Gibbs energy of formation of the target species is determined, the temperature dependence and the other thermochemical properties can be computed from the available species-specific information. The thermochemical information for the chemical species under consideration is then frozen, and used in subsequent steps as a constant. This stepwise process usually follows "the standard order of elements" (oxygen, hydrogen, Noble gases, halogens, chalcogens, pnicogens, the carbon group, etc). It appears that the "standard order" may have initially been simply intended as a convenient sorting order for the chemical species[12,13] (following the system adopted by the international critical tables), but it was afterward realized that, with small modifications, there were some advantages in using it also as the actual order for developing the thermochemical tables. The "standard order" strategy was fully exploited by the NBS tables[14] and their predecessor[15] and followed by several other thermochemical tabulations.[1,3]

Although the "standard order of elements" strategy may indeed help alleviate some of the inherent problems of the sequential process, the traditional approach produces a tabulation that has a number of difficulties. The most serious problem is the maze of hidden progenitor-progeny dependencies across the tabulation. Consequently, tabulations that were obtained by a traditional sequential process are nearly impossible to update with new knowledge. At best, one can use new species-interrelating data (such as a new measurement of some bond dissociation energy) to update the properties of one species, which is tantamount to revising or modifying one of the steps in the middle of the original sequence that produced the tabulation. Although this perhaps improves things locally (for the chemical species in question), it immediately introduces new inconsistencies across the tabulation. Namely, there will generally be other species in the table that are pegged directly or indirectly to the old value of the revised species and also need to be updated. Which those may be is far from obvious. Other difficulties, such as the potential to develop hidden cumulative errors, are caused by lack of corrective feedback to the thermochemistry of species that have been determined in previous steps and then frozen. In addition, the traditional sequential process generally produces uncertainties that are not necessarily properly quantified, since they tend not to reflect the information content that is being used in other parts of the tabulation. It can be argued that, even under the best of circumstances, the traditional sequential approach exploits only partially the available information.

3. Thermochemical Network Approach

In reality, the species-interconnecting determinations form a thermochemical network (TN). A clear realization that this is the case,[16] together with some pioneering work pointing out the need for preconditioning the TN,[17] occurred a long time ago but was not further developed and utilized in earnest. For example, the NBS tables[14] extensively discuss TNs and their importance but, as they explicitly state, in the end use the sequential method for "almost all" species, except for "the evaluation of properties of the compounds of Li and Th, and for some of the evaluations of compounds of U, Na, K, Rb, and Cs", where they use what they term "computer-assisted simultaneous solution". The JANAF tables[2] have also used small TNs in at least two cases,[18,19] whereas Cox et al.[1] have used a TN to determine the CODATA recommendations for the thermochemistry of 16 aqueous ions. Another compilation that appears to have used a computerized database of species-interrelating information is that of Pedley et al.[6] We will make further comments on these early uses of TNs later in this discussion.

Figure 1 is a graphical representation of a simple TN (which happens to be a minute subset of the TN utilized in the present

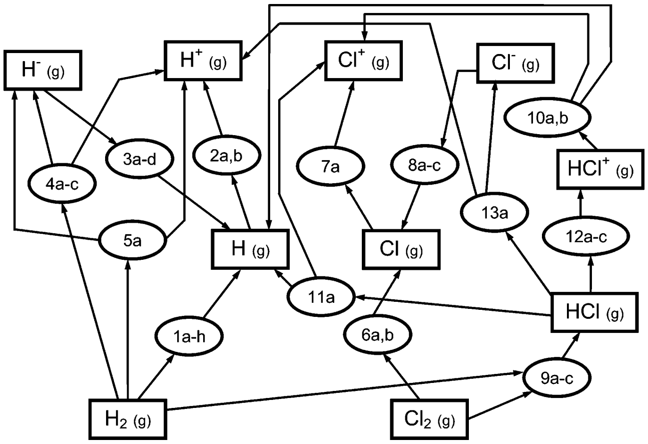

Figure 1. Graphical representation of a small subset of the current TN illustrating the topology for some of the key species described in this paper. In graph-theoretical language, the TN contains 1 primary vertex (rectangles) and 13 secondary vertices (ovals). The primary vertices represent the enthalpies of formation of various chemical species that are to be determined by solving the TN. The secondary vertices represent the chemical reactions for there are measurements of thermochemically relevant quantities. The directed edges (arrows) indicate participation in chemical reactions. The weights of the edges (not indicated explicitly) are governed by the underlying stoichiometry. Note that the edges always connect a primary vertex to a secondary vertex; first neighbor vertices are always of a different kind and second neighbors are always the same kind. Most of the secondary vertices have multiple degeneracies shown by the number-letter combinations. These degeneracies correspond to competing determinations of thermochemical properties of the same chemical reaction. For example, the oval in the lower right corner, representing the gas-phase reaction $^{1}/_{2}\,H_2 + {}^{1}/_{2}\,Cl_2 \rightarrow HCl$, is labeled 9a, 9b, and 9c, corresponding to three separate calorimetric determinations[130−132] of the enthalpy of combustion of hydrogen in chlorine to form gaseous HCl. The figure also illustrates the fact that, in general, there are multiple (alternate) pathways through the network between two arbitrarily selected primary vertices. The traditional sequential approach to thermochemistry proceeds through the network in a series of steps, each step selecting a particular path to the next primary vertex and ignoring all other paths. Each primary vertex is "solved" on the first visit, and never revisited again. The process utilizes only partly the wealth of information contained in the network. As opposed to this, the ATcT approach is based on considering simultaneously all existing pathways, hence making the best possible use of the information content.

paper). In graph-theoretical language, the TN is here depicted by a labeled graph containing two types of vertices. The primary vertices (shown as rectangles) represent the enthalpies of formation of species that need to be determined, whereas the secondary vertices (shown as ovals) represent the chemical reactions for which relevant measurements are available. In general, secondary vertices may have multiple degeneracies (reflecting competing determinations on the same chemical reaction): each of the number/letter combinations contained in the ovals in Figure 1 references one thermochemically relevant species-interrelating determination at a particular temperature. In the example depicted in Figure 1, there are 10 primary vertices (chemical species), and 13 secondary vertices (chemical reactions), with a sum degeneracy of 34 (the total number of determinations involved in this TN). The directed edges (arrows) define participation in the chemical reactions, and the weights of the edges (not explicitly labeled in Figure 1) reflect the underlying stoichiometry. Since the edges always connect a primary and a secondary vertex, first-neighbor vertices are always of a different kind, and second neighbors are always of the same type. The overall topology of the graph is driven by the reactions/measurements it describes, which fixes the weights for the edges and defines which vertices can ever become first and second neighbors.

The graph representing the TN can be mapped onto one adjacency matrix and four or more column vectors. The columns and rows of the adjacency matrix correspond to primary and secondary vertices (with each degenerate component forming a different row). The elements of the adjacency matrix reflect the weight and direction of the edges, i.e., the underlying stoichiometry. All column vectors have the same number of rows as the adjacency matrix. The elements of the first two column vectors contain the values and the adjunct uncertainties of the species-interrelating determinations, the third column vector contains the temperature at which the determination is made, and the other column vectors contain information on the type of measurement, reference(s), annotations, etc. (typical metadata, to use the computer-science lingo). It should be also noted that the removal of primary vertices that are considered fixed (such as reference elements in their standard states), coupled to the modifications of the column vectors as necessary (see Appendix), is a legitimate procedure in handling the graph.

The adjacency matrix and the first two vectors correspond algebraically to a system of weighted linear equations. The adjacency matrix is sparse, and the system is typically heavily overdetermined (the number of secondary vertices including all degeneracies normally exceeds the number of primary vertices). The excess degrees of freedom arise both from the fact that the number of chemical reactions for which thermochemically relevant measurements are known normally exceeds the number of species considered and from the fact that there will be often multiple competing measurements for the same chemical reaction.

Here it should be parenthetically noted that throughout the present paper we are using the "stationary electron convention", which is adopted in most papers involving gas-phase ion thermochemistry. Consequently, in the TN of Figure 1, the electrons balancing the chemical reactions that involve ionic species are not shown explicitly. (Although indiscriminate mixing of values belonging to different conventions inevitably leads to grave errors, the conversion from the "stationary electron convention", aka "ion convention", to the alternative "thermal electron convention", which is used for example in the JANAF tables[2] and in Gurvich et al.,[3] is rather trivial, and amounts to simply adding to each determined enthalpy of formation the quantity $2.5qRT$, where q is the charge in units of elementary charge, R is the molar gas constant, and T is the temperature; obviously the values at 0 K for charged species and at all temperatures for neutral species are the same under both conventions.)

The TN represented in Figure 1 corresponds to an ab ovo TN (aka *global* TN), where all primary vertices, except for reference elements in standard states (in the current example H_2 and Cl_2 at the bottom of the graph), are treated as unknowns. Another variant is a *local* TN, obtained by removing the primary vertices for which solutions are considered to be firmly known from prior considerations. When localizing the TN, the aim is to produce a smaller disjoint sub-graph, which can be then treated separately. Although treatment of global TN should be the preferred approach, the use of local networks can be useful in some cases.[20,21] In fact, the "computer-assisted simultaneous solution" used in the aforementioned cases in the NBS tables[14] and in the JANAF tables,[2] consisted of a judicious use of small local TNs. Obviously, during the sequential evolution of the compilation, the manual selection of the "best" species-interrelating determinations must have at times proved extremely challenging if not outright impossible because of strong interdependences within some group of species, and hence the one-species-at-a-time sequence was temporarily modified to entertain a block of related chemical species, described and solved via a local TN.

Even a brief visual examination of the graph in Figure 1 immediately reveals that there are many allowed paths through the graph between two arbitrarily selected primary vertices. The traditional sequential approach is tantamount to judiciously selecting the "best" path (based on the objective or perceived quality of the available species-interrelating determinations) and elaborating a "passage" through the network piece by piece. Noting that the sequential procedure starts always at a reference element in a standard state (which can be removed from the graph), each of the steps generally corresponds to selecting a trivial subgraph consisting of one secondary vertex and one adjunct primary vertex, solving the associated (single) linear equation for the primary vertex in question, fixing the solution, and then removing the primary vertex from the network (together with any secondary vertices that may become disjoint during the procedure). Of necessity, the sequential approach uses only a small subset of possible paths through the network, and many of the secondary vertices are either ignored or used only as a secondary confirmation. To put this in a different perspective, the traditional approach corresponds to finding a passage through the TN by elaborating and solving a sequence of forced highly localized TNs, each usually having a primary vertex cardinality of 1. The implied justification is that the sequence can be judiciously elaborated in such a way that the cross-correlations between the forced local TNs are negligible.

However, the inherently optimal set of solutions for the TN is obtained not by judiciously selecting one or another path but by considering all paths, properly weighted by their associated uncertainties. This is true irrespective of the fact that some of the secondary nodes in the TN (and hence the associated alternate pathways through the network) may indeed provide only a modest cross-correlation. The underlying mathematical problem appears to be quite simple: a simultaneous solution of a weighted overdetermined system of linear equations. This can be nominally accomplished by minimizing a suitable statistical measure, such as χ^2, provided that the adjunct uncertainties, which are used as inverse linear weights (see Appendix), are an honest representation of the underlying confidence in the species-interrelating determination present in the TN and hence provide reasonable (i.e., statistically significant) weighting for the equations. The latter is a crucial condition that needs to be fulfilled in order to obtain the optimal set of solutions. Clearly, if this is not the case, "optimistic" uncertainties will create disproportionally weighted secondary nodes (i.e., outliers), which will skew the solutions. Hence, the final simultaneous solution in weighted space needs to be, at the minimum, preceded by some form of statistical analysis that will precondition the TN by detecting and correcting possible "optimistic" uncertainties. It should be noted here that the notions of "bad" determinations and "optimistic" uncertainties are, at least for the purpose of the present discussion, interchangeable to a surprisingly large degree. This is by way of saying that the influence of a "bad" determination on the final solutions can be, for all practical purposes, entirely eliminated if its adjunct uncertainty is made sufficiently large. Although we are definitely not advocating the deliberate inclusion of measurements that are knowingly "bad" or otherwise unreliable in the TN, we would like to point out that the straightforward approach of simply disregarding such measurements, normally practiced in the manual sequential approach, is tantamount to making their uncertainties infinitely large. Though, unfortunately, one can find in the literature any number of questionable thermochemical determinations, in practice, a fair number of measurements will tend to be only somewhat off, i.e., have only slightly "optimistic" uncertainties. These determinations can still usefully contribute to the TN if their inherent uncertainties can be evaluated in some reasonable manner. Here it should be also noted that the traditional procedure of selecting one "best" determination and disregarding other available information (which may not necessarily be "bad", but maybe just slightly less "good" than the selected "best") curtails the potential of expressing the inherent confidence in the final result via a properly formed uncertainty. Namely, as long as they are at least somewhat confirmatory (rather than divergent), competitive determinations should, in general, produce an overall uncertainty that is smaller than any of the individual uncertainties, more so if the individual uncertainties are similar, and less so if they are disparate. Mutatis mutandis, the same statement applies to alternative pathways that exist within a TN.

Clearly, the care exercised during the initial accumulation of thermochemical data (both species-interrelating and species-specific) that will define the secondary nodes is a crucial ingredient defining the quality of the final thermochemical quantities. Each datum needs to be examined and critically evaluated with utmost care. The suitability of the method, approach, and procedure needs to be assessed, and, if necessary (and possible), the original data needs to be reinterpreted. Quite importantly, the overall uncertainty of the determination also needs to be determined. Here the evaluator generally relies on the uncertainty reported by the original author(s) only with great caution. There are two principal reasons for this. The first is that the evaluation of uncertainties (particularly those arising from systematic errors) is notoriously difficult, in many cases relying on the experience of the authors, rather than on some objective statistical measure that can be readily computed,[22] resulting in determinations that are sometimes reported without explicitly declaring any uncertainty, and sometimes by unwittingly declaring uncertainties that are "optimistic". The second reason is that the standard for reporting uncertainties is far from being uniform. The accepted golden paradigm in thermochemically relevant determinations, introduced by Rossini in 1931,[23] is that of reporting the 95% confidence interval (equivalent to two — or more, depending on the number of trials — standard deviations), but some authors simply report what they determine or believe to be one standard deviation, in many cases even without explicitly saying so. The notoriously burdensome process of critical evaluation of the initial data, which relies to the highest degree on the experience and soundness of judgment of the evaluator, is common to all procedures and is a necessary (but not a sufficient) condition to derive reliable final results, irrespective of whether a sequential method will be applied or the TN will be used. It should be noted here that the goal of this initial step is to extract the best possible value for the determination from data that comes as close as possible to the originally measured (or computed) quantities and to evaluate its accuracy and reliability by taking note both of the known details of the determination and of the overall experience concerning the method, but without directly comparing the currently evaluated determination to other similar (independent) determinations. The comparison of similar determination is best performed during the next step, described below.

Once the data is assembled, the mutual consistency of various pieces of information needs to be evaluated. At this point, the procedures diverge, depending on the approach taken. In the sequential approach, this is the step in which the evaluator juxtaposes all available data related to a target species and decides either which is the "best" determination, or which subset of determinations should be used through some averaging procedure. With a TN,, a totally new set of possibilities opens up. Namely, if all data in a TN were self-consistent, alternative paths through the TN would produce solutions that do not differ by more than the underlying cumulative uncertainty. In principle, one could imagine checking all closed loops that exist in a TN. Along any closed cycle, the sum of the relevant thermochemical quantity should equal to zero within the propagated uncertainty. If it does not, this indicates that at least one of the determinations involved in that loop has an "optimistic" uncertainty. If there is sufficient redundancy in the various loops, this allows the isolation of the suspect determination(s). One can then try to augment the adjunct uncertainty of the suspect determination and repeat the exercise until self-consistency is achieved. In fact, we have earlier successfully preconditioned TNs during manual or semi-manual treatments by applying exactly this kind of strategy.[20,21]

The procedure used by the NBS tables[14] for select blocks of local TNs, as outlined by Garvin et al.,[17] has employed a combination of a computerized "linear analysis" and manual intervention to precondition the species-interrelating data. As opposed to this, Pedley et al.[6] have apparently pre-selected "definitive" measurements entirely manually. (Since Pedley et al. have not employed a least-squares final optimization, and since in most cases they either selected only one "definitive" measurement per species, or, when multiple competing measurements were selected, they were very similar, their procedure in many aspects resembles a computer-assisted sequential procedure.) The general strategy utilized in the JANAF tables in those instances where local TNs were employed was presumably intended to be similar to what was used in the NBS tables. However, at least in the instance that was reanalyzed in some depth in this laboratory,[20] the JANAF procedure simply skipped the self-consistency check of the local TN "for lack of time",[18] which led to severe inconsistencies in the final enthalpies of formation.[20]

We are currently in the process of developing various algorithms that analyze the topology of the TN, and, in conjunction with that effort, we are also investigating strategies that may lead to automated loop-check approaches. However, explicit loop-checking may not be necessary. Namely, we have currently implemented in ATcT an automated "worst offender" analysis that appears to be a shortcut either equivalent or very similar to the loop-check approach, and has produced very satisfactory results in preconditioning the TN.

In this iterative "worst offender" approach, "trial" solutions for the primary nodes in linearly error-weighted space (i.e., a space where all uncertainties have a value of unity) are computed by solving the TN and then used to calculate the "trial" values for the secondary vertices. The computation of the "trial" values for the secondary nodes, of course, makes use of the proper stoichiometric relationships. These "trial" values are compared to the original values, and a ranked list of potential "offending" secondary vertices is created. The "offending rank" is based on the discrepancy between the original value and the "trial" value. In the current implementation of the "worst offender" strategy, the focus is on the direct deviation between the "trial" and the original value, making use of the fact that in the linearly weighted workspace the original uncertainties of the secondary vertices are unity (which simplifies the numerical procedure). Though computed, the additional information hidden in the full covariance matrix is not presently used to additionally refine this evaluation. (The use of the additional information present in the full covariance matrix and in the matrix containing sensitivity coefficients to perform more complex evaluation procedures will be explored in future expansions of the ATcT code.) The uncertainty of the current top-ranking "offender" is then slightly expanded (by an externally adjustable amount, set currently by default to about two percent), and a new iteration is attempted. The procedure is repeated until the TN is self-consistent. The current implementation of the "worst offender" procedure has two somewhat conservative (and perhaps not entirely necessary) safeguards: only one "worst offender" (or the top tier of equivalent "worst offenders") is corrected during any iteration, and even then, the adjunct uncertainty is enlarged by a relatively small amount. Namely, the existence of a highly "optimistic" uncertainty has a tendency to skew the "trial" result, and hence, it is inherently unfair to use such a result to evaluate any secondary nodes other than the "worst offender". Also, enlarging the uncertainty in very small (repetitive) steps ensures that no uncertainty is amplified significantly beyond the value that is really necessary to achieve a self-consistent TN.

Here it should be stressed that the isolation of "offenders" is made possible by the presence of alternative paths and competing measurements in the graph. (If there are no alternative paths through the TN, nor competing measurements, then, just as in the case of the traditional approach, the only possible corrective action comes from the intuition and insight of the evaluator assembling the initial data and setting accordingly the initial uncertainty of the secondary vertex.)

Once a self-consistent TN is obtained through the described "worst offender" iterative procedure, the final solutions for all primary vertices are computed and coupled to species-specific information to develop the full complement of thermochemical information.

4. Active Thermochemical Tables (ATcT)

ATcT are a newly developed software suite[24] based on the TN approach described above. Although ATcT has been designed as a self-standing application that can be run on a personal computer, it is currently also exposed through a framework of Web and Grid Services[25,26] using servers at Argonne National Laboratory. The ATcT distributed architecture is an integral part of the Collaboratory for Multi-Scale Chemical Science (CMCS),[27] and the ATcT services are currently accessible to interested pilot users via the CMCS Portal.[28]

ATcT consists of several parts: the software kernel, the underlying thermochemical database, and the user interface that connects to the ATcT services and exposes the full functionality of the ATcT within the CMCS infrastructure. The continuous development of the kernel, the user interface and the database are a long-term project currently led by Argonne National Laboratory.

The ATcT database is organized as a series of "Libraries". Each library consists of a collection of files containing various species-specific and species-interrelating data, together with information that allows unique identification of the desired chemical species. Each library also contains archival copies of all files, corresponding to snapshots of previous states of the library, taken before any major changes are made. The Core (Argonne) TN is maintained in the central library (termed "MainLibrary"). The central library also stores (and exposes to queries) the most current solutions to the Core TN, together with archival copies of previous versions. The database also incorporates several auxiliary Libraries containing non-networked data on enthalpies of formation and the related species-specific information, which are currently being extracted from popular thermochemical compilations. These auxiliary libraries are incorporated as a convenience to potential users, and are meant to provide an expedient way to compare the solutions stored in the central library to historical data. Individual users and workgroups have the opportunity to establish their own mini-libraries (termed "Notes"), in which they can store data that supplements or modifies the information contained in the central and auxiliary libraries.

The ATcT kernel is the computational workhorse. The central functions of the kernel are the construction, manipulation, and solution of TNs, and data query and retrieval. The queries entertain requests for thermochemical information for a single chemical species, for a chemical reaction, or for a supplied list of species/reactions. The input parser decides whether the user has requested an action (such as indicating a change in some user-settable parameters or initiating a new solution to a TN) or a query, whether the query was for a species or for a chemical reaction, whether the query-term(s) were species names, formulas, or some other identifiers, such as CAS numbers, whether a particular aggregate state was specified (gas, crystal, liquid, aqueous at infinite dilution or at some other dilution, etc) or not, etc. The user can dynamically configure the query modalities, such as request a tailored search sequence through libraries/notes and can customize a number of output parameters, such as define the schedule for which the temperature-dependent functions should be provided, change the displayed units, etc. Queries attempt to deliver a table of standard thermochemical information, including enthalpies of formation, Gibbs energies of formation, heat capacities, entropies, enthalpy increments, and equilibrium constants, for the desired combination of temperature(s), together with relevant pedigree-type information. The user-configurable search sequence defines which library should be considered as the source of the "preferred" value for the enthalpy of formation. Although all relevant enthalpies of formation that are found in the libraries are displayed, the "preferred" value (which, in the case of the central library is based on a TN solution) is the starting point for building the displayed table of information, which is calculated in real time from the available species-specific information. The temperature-dependent information is normally generated from the highest-level species-independent information found in the examined libraries. For gas-phase species, the displayed information is based on ideal-gas thermochemistry. If data exists, the partition function-related properties are calculated by direct counting from stored lists of energy levels or from the available spectroscopic constants. If such information is lacking, or for condensed-phase and aqueous species, the information is derived either from stored discrete tables containing heat capacity, entropy, and enthalpy increment data for a set of temperatures, or, if all else fails, from stored polynomials. In case of tabulated data, when information is requested for intermediate temperatures that are not stored explicitly in the database, the heat capacity data is obtained by spline-interpolation of the existing entries, and the other properties are derived by computing the appropriate incremental integrals of the heat capacity, starting from the closest stored entry.

Although serving the desired thermochemical information through queries is the utilitarian end service, the real raison d'être of ATcT is the capability of handling and solving TNs. In a normal state of affairs, the library that contains a TN also contains its current solution, and hence queries for the latest thermochemical information simply scrutinize the stored solution. When the content of the library is updated with new information, such as new species-interrelating determinations or new species-specific information that may affect the TN, a new solution to the TN can be requested by the owner or caretaker of the library. When such action is initiated, ATcT creates an archival snapshot of the current state of the library and proceeds by examining all information existing in the library and constructing the TN. With few exceptions, the species-interrelating information that defines the secondary vertices is stored in the library in a form that is tightly related to the original type of determination and to the original temperature, and can be interpreted as (or readily converted to) an enthalpy or Gibbs energy of reaction. The stored information also includes a specification as to the meaning of the adjunct uncertainty (95% confidence limit intervals is the default, but that can be changed by the user globally and/or for any individual secondary vertices), and additional external weights, if any. The initial TN is then manipulated by utilizing the best available species-specific information to convert all secondary vertices to one and the same type of quantity (enthalpy of reaction is the currently fully implemented choice) at one and the same temperature (selectable, with 298.15 K being convenient, particularly if aqueous thermochemistry is also involved, and 0 K being another standard choice). The next step is the removal of all fixed primary vertices. These are normally limited to elements in their reference states, but the user can specify otherwise. In the latter case, the affected secondary nodes are also modified: depending on whether the fixed primary vertex was a reactant or a product connecting to the affected secondary vertex was connected, the enthalpy of formation of the fixed vertex, scaled by the appropriate stoichiometric factor, is either added to or subtracted from the value for the secondary vertex and the associated uncertainty of the fixed enthalpy of formation is propagated accordingly to the overall uncertainty of the secondary node. Once all fixed primary vertices are removed, the topology of the TN is analyzed to isolate disjoint sections, which are then solved separately. During this whole procedure, the TN graph is handled by manipulating its adjacency matrix and the associated column vectors that contain the original and modified values and uncertainties, augmented by relevant metadata linking the primary and secondary vertices to information stored in the database. In lieu of the fully expanded (sparse) adjacency matrix, the algoritms operate on a condensed representation that takes advantage of its sparseness.

At this point, the problem can be numerically treated using standard approaches appropriate to an overdetermined system of linear equations (see Appendix). Note that ATcT checks if the system of equations is indeed a tractable overdetermined system and, if not, notifies the user. (The system will obviously be intractable if it is underdetermined, but also if the TN is "floating", i.e., lacks sufficient direct or indirect reference to elements in their reference states.) If the system is tractable, the "worst offender" procedure, explained above, is iteratively applied until the TN becomes self-consistent. During each iteration, the equations are linearly weighted using the associated uncertainties of the secondary nodes (some of which are being additionally modified as the "worst offender" procedure evolves). Once weighted, the manipulated adjacency matrix has become the design matrix of the optimization problem, from which the standard normal equations of the least squares problem can be determined, producing by inversion the covariance matrix and the solutions. When the TN becomes self-consistent, the final solution can be computed by the same procedure. The uncertainties of the final solutions are extracted from the covariance matrix, modified to reflect the desired meaning (95% confidence limit is the default, but the user can request a different uncertainty quantification), and stored together with the relevant metadata.

5. Core (Argonne) Thermochemical Network

The central library of the ATcT database contains the Core Thermochemical Network. The current version (1.033) has nearly 850 species-interrelating determinations, involving some 250 thermochemical species, and is growing on a daily basis.

In the remainder of this section, we will highlight the determinations that are used to define the secondary vertices of the initial TN and are relevant to the illustrative results given in Section 6. The associated comments are intended to give only the most pertinent details of the underpinning critical evaluation that was applied at this stage of initial accumulation of information.

The reader should be reminded that the determinations listed below are simply a starting point from which ATcT takes over. As mentioned earlier, one of the differences between the sequential approach and the ATcT approach is that the manual critical evaluation of the data is limited to ensuring the quality and integrity of the initial data, and does not concern itself with solving potential inconsistencies in the TN, i.e., does not attempt to manually compare competing measurements nor evaluate alternate cycles that are possible within the TN. Rather, this is accomplished by ATcT. The processing and solving of the TN by ATcT involves a large number of additional manipulations, some of which detect and address potential inconsistencies in the TN, as described earlier in this paper. Hence, the purpose of this section is to simply fulfill the need of clearly documenting and pedigreeing the starting state of the TN.

The reader should also note that in the ATcT Core TN the originally reported units are generally preserved (with the exception of outdated units, such as international Joules or mean calories). Hence, the various values quoted in this discussion are usually given in the original units and are occasionally parenthetically converted to the other prevalent units for the same quantity as a help to the reader.

5.1. $D_0(O_2)$. The TN contains the determination of $D_0(O_2)$ by Brix and Herzberg[29,30] that was used in the CODATA evaluation,[1] as well as more recent data.[31–33] The CODATA value for $\Delta_f H^\circ_{298}$(O) is based on the value of $D_0(O_2) = 41260 \pm 15$ cm^{-1} given by Brix and Herzberg,[30] and has been adopted by JANAF,[2] Gurvich et al.,[3] and other compilations. However, it should be noted that Brix and Herzberg[30] refer their value (and explicitly state so) relative to the nonexistent level $v = 0$, $N = J = 0$ of X $^3\Sigma_g^-$. It should be also noted that the thermochemically relevant value of D_0 needs to refer to the lowest *existing* level of the molecule, which can be easily derived by taking into account both the lowest possible value of J and the nuclear spin statistics. Brix and Herzberg also explicitly say that the stated uncertainty is "conservative". The origin of the value is from their D_0(O$_2$, B $^3\Sigma_u^- \rightarrow$ O $^3P_2$ + O $^1D_2$) = 57127.5 ± 5 cm^{-1}, based on a Birge-Spooner extrapolation using $v = 0-21$. Taking the currently available[34] term value for O $^1D_2$ of 15867.862 cm^{-1} produces the dissociation energy of O$_2$ of 41259.6 ± 5 cm^{-1}, which is still referred to the nonexistent level $v = 0$, $N = J = 0$ of X $^3\Sigma_g^-$. The lowest level of O$_2$ X $^3\Sigma_g^-$ that is not wiped out by nuclear spin statistics of $^{16}O_2$ is $N = 1$, $J = 0$ (F_3 term), with a term value of -1.09 cm^{-1}, as calculated from the constants given in Huber and Herzberg[35] and using Schlapp formulae[36] (and also as reported by Cosby and Huestis[33]). This increases $D_0(O_2)$ to 41260.7 ± 15 cm^{-1}. Note that in their earlier report[29] Brix and Herzberg indeed gave 41261 ± 15 cm^{-1}. For some reason, CODATA Key Values (and other tables) do not make this additional 1 cm^{-1} correction. Admittedly, this is a very small correction compared to the associated ±15 cm^{-1} uncertainty, but it brings the determinations of Brix and Herzberg slightly closer to the more recent determinations. Lewis et al.[31] reinterpreted the data of Brix and Herzberg[30] by attributing previously unassigned discrete absorption features of O$_2$ to B $^3\Sigma_u^-$ ($v = 22$) $\leftarrow$ X $^3\Sigma_g^-$, as indeed originally suggested by Brix and Herzberg. The extended set leads to D_0(O$_2$,B $^3\Sigma_u^-$) = 57135 ± 3 cm^{-1}, which is 7.5 cm^{-1} higher than the original Brix and Herzberg[30] value and translates to D_0(O$_2$, X $^3\Sigma_g^-$) = 41268.2 ± 3 cm^{-1}. More recent determinations of $D_0(O_2)$, corrected to refer to the lowest existing level of O$_2$, are as follows: from Lewis et al.[31] (41269.2 ± 0.5 cm^{-1}), Gibson et al.[32] (41269.6 ± 0.9 cm^{-1}), and Cosby and Huestis[33] (41268.6 ± 1.1 cm^{-1}). Cosby and Huestis[33] give a good analysis of all of the data available on the dissociation energy of O$_2$. They also comment that there is a discrepancy between the term values of Lewis et al.[31] and Gibson et al.[32] of up to 0.7 cm^{-1}, as well as a discrepancy between spectroscopic and positive ion cycle results (involving determinations listed below).

5.2. Electron Affinities and Ionization Energies of O and O$_2$. The ionization energy of O, IE(O), is taken from Eriksson and Isberg[37] (109837.02 ± 0.06 cm^{-1}), with the addition of the less accurate but confirmatory direct observation by Dehmer et al.[38] ($13.618_1 \pm 0.001_4$ eV = 109837 ± 11 cm^{-1}).

The values for the electron affinity of O, EA(O), are from Neumark et al.[39] (11784.645 ± 0.006 cm^{-1}, a value repeated in Hotop and Lineberger[40]), Blondel,[41] (11784.648 ± 0.006 cm^{-1}, which is a slight correction of the value of Neumark et al.[39]), and Valli et al.[42] (11784.682 ± 0.020 cm^{-1}).

The ionization energy of O$_2$, IE(O$_2$), is from Dibeler and Walker[43] (12.072 ± 0.008 eV = 97367 ± 65 cm^{-1}), Edqvist et al.[44] (12.071 ± 0.020 eV = 97360 ± 160 cm^{-1}), Dehmer and Chupka[45] (12.074 ± 0.007 eV = 97383 ± 56 cm^{-1}), Samson and Gardiner[46] (97361.5 ± 9.5 cm^{-1}), Tonkyn et al.[47] (97352 ± 2 cm^{-1}), Kong and Hepburn[48] (97351.0 ± 1.3 cm^{-1}), and Song et al.[49] (97345 ± 5 cm^{-1}, recalculated from their constants). The last three determinations have been additionally adjusted to refer to the lowest existing level of O$_2$.

The electron affinity of O$_2$, EA(O$_2$), is from Celotta et al.[50] (0.43 ± 0.03 eV), Burrow[51] (0.45 ± 0.03 eV) and Travers et al.[52] (0.451 ± 0.007 eV).

5.3. Additional Determinations Involving O$_2$. The 0 K ion-pair formation threshold, IPF(O$_2$), corresponding to the heterolytic bond dissociation $O_2 \rightarrow O^+ + O^-$, is from Dehmer and Chupka[45] (139316.6 ± 9.7 cm^{-1}; corrected from their reference level $J = 1$ − assumed here to correspond to the F_2 term − to the lowest existing level of O$_2$) and from Martin and Hepburn[53] (139321.2 ± 0.7 cm^{-1}, also corrected from their reference level N = 1, $J = 2$ to the lowest existing level of O$_2$).

The 0 K appearance energy of O$^+$ from O$_2$, AE(O$^+$/O$_2$), corresponding to the dissociative ionization process $O_2 \rightarrow O^+ + O + e^-$, comes from a variety of sources. Albritton et al.[54] (151100.2 ± 9.2 cm^{-1}, referred to the lowest existing level of O$_2$), have determined the dissociation energy of O$_2^+$ from b $^4\Sigma_g^-$ ($v = 0$, $N = 1$, F_4), and utilized the kinetic energy release measured by Tadjeddine et al.,[55] the appropriate term value of Albritton et al.,[56] and the origin-corrected ionization energy of O$_2$ to O$_2^+$ b $^4\Sigma_g^-$ of Yoshino and Tanaka.[57] Cosby and Huestis[58] (151094.7 ± 2.6 cm^{-1}, referred to the lowest existing level of

O_2) have also determined the dissociation energy of O_2^+ from b $^4\Sigma_g^-$ ($v = 0$, $N = 1$, F_4) and utilized the kinetic energy release measured by Pernot et al.,[59] the appropriate term value from Cosby et al.,[60] and the aforementioned ionization value of Yoshino and Tanaka.[57] The origin correction of the Rydberg series observed by Yoshino and Tanaka has been criticized and revised by Cosby et al.;[60] with this correction, the two aforementioned values for AE(O^+/O_2), based on data from Albritton et al.[54] and Cosby and Huestis[58] become higher by about 16 cm^{-1} (151116 ± 10 cm^{-1} and 151111 ± 6 cm^{-1}, respectively). Finally, a yet different value for the ionization energy of O_2 to O_2^+ b $^4\Sigma_g^-$ can be obtained from the determination of the ionization energy of O_2 to O_2^+ a $^4\Pi_u$ by Kong and Hepburn,[61] combined with ν_{00} for O_2^+ b $^4\Sigma_g^- \leftarrow$ a $^4\Pi_u$ from Huber and Herzberg.[62] With this third choice, the values for AE(O^+/O_2) based on data from Albritton et al.[54] and Cosby and Huestis[58] become higher than the first set by about 6 cm^{-1} but lower than the second set by about 10 cm^{-1} (151105.9 ± 9.2 cm^{-1} and 151100.4 ± 2.6 cm^{-1}, respectively). All of the above values have been incorporated in the TN, together with the determination of AE(O^+/O_2) by from Blyth et al.[63] (18.733 ± 0.016 eV = 151090 ± 130 cm^{-1}, a weighted average with 95% confidence limits of their ionization energies, corrected for the kinetic energy release and average thermal rotational energy of the parent of approximately 0.025 eV). In addition, we have included a value that has a rather unclear pedigree but is quoted by Hsu et al.[64] and again by Song et al.[65] (18.733 ± 0.003 eV = 151092 ± 24 cm^{-1}).

The charge-exchange ion−molecule reaction $O^- + O_2 \rightarrow O + O_2^-$ has been studied by Celotta et al.,[66] who found that the difference between the two electron affinities is 1.025 ± 0.008 eV.

5.4. Determinations Relating to O_3, O_3^+, and O_3^-. The determinations of the equilibrium $^3/_2\ O_2 \rightarrow O_3$ are from Kailan and Jahn[67] (34.5 ± 1.0 kcal/mol at 294 K, 144.3 ± 4.2 kJ/mol), Clyne et al.[68] (33.7 ± 0.2 kcal/mol at 298 K, 141.00 ± 0.84 kJ/mol), and a reinterpretation (apparently similar, if not identical, to that performed by Gurvich et al.[3]) of the determination of Gunther et al.[69] (33.9 ± 0.3 kcal/mol at 294 K, 141.8 ± 1.3 kJ/mol).

The values for the bond dissociation $O_3 \rightarrow O_2 + O$, $D_0(O_2{-}O)$, are based on the determinations of Takahashi et al.[70] (101.51 ± 0.25 kJ/mol) and of Taniguchi et al.[71] (102.46 ± 0.04 kJ/mol). Both require additional discussion.

Takahashi et al.[70] report an onset for dissociation of O_3 to O ^{1}D and O_2 a $^1\Delta_g$ of 310.2 ± 0.2 nm (= 32237.3 ± 20.8 cm^{-1}). They combine it with ν_{00} of O_2 X $^3\Sigma_g^- \leftarrow$ a $^1\Delta_g$ of 7882.39 cm^{-1} from Herzberg and Herzberg[72] (also reported in Huber and Herzberg[62]) and with the O ^{1}D term of 15867.7 cm^{-1} to obtain $D_0(O_3) = 101.53 \pm 0.25$ kJ/mol. Takahashi et al. do not state explicitly to which level of O_2 a $^1\Delta_g$ their onset refers to, but, since it corresponds to a threshold in a real spectrum, one would assume that it refers to the lowest existing level, $J = 2$. The band head ν_{00} of Herzberg and Herzberg refers to the origin of the relevant expressions for rotational terms, i.e., to the hypothetical transition X $^3\Sigma_g^-$ ($v = 0$, $J = 0$) ← a $^1\Delta_g$ ($v = 0$, $J = 0$) of O_2. The actual transition involving the lowest existing levels in O_2, X $^3\Sigma_g^-$ ($v = 0$, N = 1, $J = 0$, F_3) ← a $^1\Delta_g$ ($v = 0$, $J = 2$) is almost 10 cm^{-1} larger, 7892.05 cm^{-1} (from constants given by Huber and Herzberg,[62] which reproduce within 0.01 cm^{-1} the lines listed by Herzberg and Herzberg[72]). With the aforementioned interpretation of the onset, and with the O $^1D_2$ term value[34] of 15867.862 cm^{-1}, this produces $D_0(O_2{-}O) = 8477.4 \pm 20.8$ cm^{-1} = 101.41 ± 0.25 kJ/mol. If, however, the experimental onset for some reason refers to the hypothetical $J = 0$ level of O_2 a $^1\Delta_g$ (and, as we shall see below, there seem to be some indications to that effect), then the result has to be increased by 8.507 cm^{-1} = 0.10 kJ/mol, yielding 101.51 ± 0.25 kJ/mol, which is, because of cancellation of inaccuracies, only 0.02 kJ/mol lower than the original value of Takahashi et al.

Taniguchi et al.[71] report three experiments: one PHOFEX and two 2D fragment imaging measurements. The PHOFEX shows an onset of 309.45 ± 0.03 nm (= 32315.4 ± 3.1 cm^{-1}), which is, as noted by the authors, somewhat higher (78.1 cm^{-1} or 0.93 kJ/mol) than the similar experiment of Takahashi et al.[70] From the two 2D imaging experiments (one at 305.746 nm and one at 309.096 nm), Taniguchi et al.[71] report onsets of 386.59 ± 0.03 kJ/mol and 386.62 ± 0.05 kJ/mol. Combining these two with the PHOFEX onset (386.58 ± 0.04 kJ/mol), they derive a consensus value of 386.59 ± 0.04 kJ/mol, and using the same auxiliary data as before[70] (see discussion above), they derive $D_0(O_2{-}O) = 102.48 \pm 0.04$ kJ/mol. However, the analysis of the 2D imaging experiments seems to be using for the determination of the onset nonexistent rotational levels of O_2 a $^1\Delta_g$ $J = 1$ and 0. Fortunately, this appears to simply cause a linear shift, and the results can be corrected by simply adding 8.507 cm^{-1}. Proceeding along the lines of the discussion given above in conjunction with the determination of Takahashi et al.,[70] yields from the imaging experiments $D_0(O_2{-}O) = 8565.0 \pm 2.5$ cm^{-1} = 102.46 ± 0.03 kJ/mol and $D_0(O_2{-}O) = 8567.5 \pm 4.2$ cm^{-1} = 102.49 ± 0.05 kJ/mol, and from the PHOFEX experiment $D_0(O_2{-}O) = 8555.5 \pm 3.1$ cm^{-1} = 102.35 ± 0.04 kJ/mol, if that onset refers to O_2 a $^1\Delta_g$ $J = 2$. The two 2D imaging results clearly agree with each other. The PHOFEX experiment can be brought into better agreement by assuming that its onset refers to the hypothetical $J = 0$ level of O_2 a $^1\Delta_g$, and increasing it by 8.507 cm^{-1} = 0.10 kJ/mol, which yields $D_0(O_2{-}O) = 102.45 \pm 0.04$ kJ/mol. In that case, the consensus value appears to be $D_0(O_2{-}O) = 102.46 \pm 0.04$ kJ/mol, which again, because of cancellation of inaccuracies, is only 0.02 kJ/mol lower than their original value.

The 0 K appearance energy of O_2^+ from O_3, EA(O_2^+/O_3) = 13.125 ± 0.004 eV, corresponding to dissociative ionization $O_3 \rightarrow O_2^+ + O + e^-$, is from Weiss et al.[73]

The study of Weiss et al. also provides IE(O_3) = 12.519 ± 0.004 eV. Other congruent but slightly less accurate values for the ionization energy of O_3 are from Frost et al.,[74] Radwan and Turner,[75] Dyke et al.,[76] and Brundle.[77]

The electron affinity determinations of O_3, EA(O_3), are from Novick et al.[78] (16960 ± 20 cm^{-1} = 2.1028 ± 0.0025 eV), Arnold et al.[79] (2.103 ± 0.004 eV), and Wang et al.[80] (2.082 ± 0.040 eV).

5.5. $D_0(H_2)$, $D_0(D_2)$, and D_0(HD). The enthalpy of formation of the H atom, as determined by Cox et al.,[1] and accepted by all other compilations, is based on $D_0(H_2) = 36118.3 \pm 1$ cm^{-1}, nominally from Herzberg.[81] In that paper, as well as in an earlier paper,[82] Herzberg finds that $D_0(H_2)$ is less than 36118.3 cm^{-1} and larger than 36116.3 cm^{-1} (see Table 1 in ref 82 and Table 3 in ref 81), where the lower limit is higher than the even earlier value of Herzberg and Monfils[83] (36113.6 ± 0.3 cm^{-1}). Herzberg[81] also provides evidence that the actual $D_0(H_2)$ must be close to the upper limit of 36118.3 cm^{-1}. Cox et al.[1] have interpreted this to mean 36118.3 ± 1 cm^{-1}. The TN contains also other determinations of $D_0(H_2)$, both older and newer. The older determination is from Beutler[84] (36116 ± 6 cm^{-1}), and the newer ones are from Stwalley[85] (36118.6 ± 0.5 cm^{-1}), McCormack[86] and McCormack and Eyler[87] (36118.2$_6$ ± 0.2

cm^{-1}; ref 87 lists the dissociation limit to H 1s$_{1/2}$ + H 2s$_{1/2}$ from ref 86 as 118377.2 ± 0.2 cm^{-1}, which can be combined with the 2s$_{1/2}$ term value of 82258.942 cm^{-1} from Moore[88]), Balakrishnan et al.[89] (36118.11 ± 0.08 cm^{-1}), Eyler and Malikechi[90] (36118.06 ± 0.04 cm^{-1}), and Stoicheff[91] (36118.06 ± 0.04 cm^{-1}; this author gives averages of values for D_0 of hydrogen and his isotopomers computed between 1983 and 1993).

For $D_0(D_2)$, the data utilized in the TN is from Herzberg and Monfils[83] (36744.2 ± 0.5 cm^{-1}, including a small correction following Stoicheff[91]), Herzberg[81,82] (36748.9 ± 0.4 cm^{-1}), LeRoy and Barwell[92] (36748.88 ± 0.03 cm^{-1}), Balakrishnan and Stoicheff[93] and Balakrishnan et al.[89] (36748.38 ± 0.07 cm^{-1}), Eyler and Malikechi[90] (36748.32 ± 0.07 cm^{-1}), and Stoicheff[91] (36748.349 ± 0.005 cm^{-1}).

Similarly, the determinations of the bond dissociation energy of HD are from Herzberg and Monfils[83] (36400.5 ± 1.0 cm^{-1}, including a small correction following Stoicheff[91]), Herzberg[81,82] (36406.2 ± 0.4 cm^{-1}), Eyler and Malikechi[90] (36405.88 ± 0.10 cm^{-1}), Balakrishnan et al.[94] (36405.83 ± 0.10 cm^{-1}), and Stoicheff[91] (36405.775 ± 0.010 cm^{-1}).

5.6. Determinations Involving Ions of H, H_2, and Their Isotopomers. The values for IE(H_2) are from Herzberg and Jungen,[95] (124417.2 ± 0.4 cm^{-1}, based on Herzberg[82]), Gilligan and Eyler[96] (124417.507 ± 0.018 cm^{-1}), McCormack et al.[97] (124417.507 ± 0.012 cm^{-1}, after readjustments by Shiner et al.[98]), and Jungen et al.[99] (124417.484 ± 0.017 cm^{-1}, after Shiner et al.[98]).

The ionization energy of D_2, IE(D_2), is from Jungen et al.[100] (124745.353 ± 0.024 cm^{-1}, after readjustments by Shiner et al.[98]) and Takezawa and Tanaka[101] (124746.6 ± 0.6 cm^{-1}).

The values for IE(HD) are from Herzberg and Jungen[95] and Takezawa and Tanaka[101,102] (124568.4 ± 0.6 cm^{-1}), Gilligan and Eyler[96] (124568.479 ± 0.020 cm^{-1}), and Gilligan and Eyler[96] after Shiner et al.[98] (124568.481 ± 0.012 cm^{-1}).

The ionization energy of H, IE(H), is from Garcia and Mack[103] (109678.764209 ± 0.01 cm^{-1}) and Erickson[104] (109678.773704 ± 0.000006 cm^{-1}). Note that in a number of reference books the value from Garcia and Mack[103] is quoted as 109678.758 cm^{-1}, following Moore.[88] According to Gurvich et al.,[3] the latter is based on a tentative pre-publication value of Mack.

The ionization energy of deuterium atom, IE(D), is from Garcia and Mack[103] (109708.607927 ± 0.01 cm^{-1}) and Erickson[104] (109708.616541 ± 0.000008 cm^{-1}).

The values for the electron affinity of H, EA(H), are from Dehmer and Chupka[105] and Hotop and Lineberger[108] (6081 ± 2.5 cm^{-1}), Pekeris[106,107] (6083.092 ± 0.01 cm^{-1}), Hotop and Lineberger,[40,108] following Aashamar[109] (6083.06 ± 0.02 cm^{-1}), and Lykke et al.[110] (6082.99 ± 0.15 cm^{-1}).

The electron affinity of D, IE(D), is from Lykke et al.[110] (6086.2 ± 0.6 cm^{-1}).

The 0 K ion-pair formation threshold of H_2, IPF(H_2), corresponding to the heterolytic bond dissociation $H_2 \rightarrow H^+ + H^-$, is from Pratt et al.[111] (two slightly different but congruent determinations, 139714 ± 3 cm^{-1} and 139711 ± 3 cm^{-1}), and Shiell et al.[112] (139714.8 ± 1.0 cm^{-1}).

The 0 K ion-pair formation threshold of D_2, IPF(D_2), is from Shiell et al.[112] (140370.2 ± 1.0 cm^{-1}).

The 0 K appearance energy of H^+ from H_2, AE(H^+/H_2), corresponding to dissociative ionization $H_2 \rightarrow H^+ + H + e^-$, is from Weitzel et al.[113] (18.078 ± 0.003 eV).

5.7. Combustion Calorimetry on H_2O. Unfortunately, high-accuracy calorimetry appears to be a dying field, and there are no new measurements relating to water.

The benchmark determination of the 298.15 K enthalpy of combustion of H_2 to form liquid water, corresponding to the reaction $^1/_2\ O_2 + H_2 \rightarrow H_2O$ (l), is due to Rossini. Data needed to extract the final value are spread over at least three papers.[114−116] In the first paper an inappropriate correction for a pressure dependence has been applied, which was corrected in the second paper. However, there were some other subtle unreported changes, producing a yet different value in the third paper, which was then implicitly reconfirmed as the believed correct value in Rossini's review.[117] To clarify things, we have retraced all the steps that have been taken by Rossini in treating the raw data (and discovered several minor numerical inaccuracies in Rossini's computations of the various averages, corrections, etc.). This recalculation, with subsequent conversion from "international Joules" to current ("absolute") Joules, and correction to the current molecular weight of water (18.0162) leads to −285.825 ± 0.040 kJ/mol, which is used in the TN. Here, the uncertainty is slightly liberal, as originally adopted by Rossini in his final result. (The actual 95% uncertainty limit, as recomputed by us is ±0.032 kJ/mol, compared to that given by Rossini, which is ±0.034 kJ/mol). Note that the value extracted by Cox et al.[1] from Rossini's work is very similar, but not identical: −285.830 ± 0.040 J/mol. A slightly less complex but otherwise similar recalculation of the more recent data of King and Armstrong[118] leads to the alternate determination of the combustion enthalpy of hydrogen (−285.67 ± 0.32 kJ/mol).

5.8. Enthalpy of Vaporization of H_2O. Rossini[116] reports a value for the enthalpy of vaporization of water at 298.15 K that has derived by taking unpublished data by Osborne, Stimson, and Ginnings on real water at reduced pressure and correcting it to the ideal state; the value used in the TN (44.012 ± 0.013 kJ/mol) has been obtained by additional corrections to current Joules and the current molecular weight of water. Additional determinations in the TN are from Haar et al.,[119] as utilized in Cox et al.[1] (44.004 ± 0.002 kJ/mol), and from Keenan et al.,[120] as utilized by Gurvich et al.[3] (44.016 ± 0.010 kJ/mol).

5.9. Ionization Energy of H_2O. The determinations of the ionization energy of water, IE(H_2O), are from Reutt et al.[121] (12.6223 ± 0.004 eV = 101806 ± 32 cm^{-1}), Page et al.[122] (101777 ± 7 cm^{-1}), Child and Yungen[123] (101772 ± 2 cm^{-1}), and Tonkyn et al.[124] (101766 ± 2 cm^{-1}).

5.10. $D_0(Cl_2)$. The bond dissociation energy of Cl_2 is taken from LeRoy and Bernstein[125] (19999.18 ± 0.3 cm^{-1}). These authors determined 19997.25 ± 0.3 cm^{-1} for $^{35}Cl_2$, which was here modified by standard isotope relationships (including the Y_{00} term) to correspond to the average atomic weight of Cl of 35.457, as customary in thermochemistry. Note that Cox et al.[1] use 19999 ± 1 cm^{-1}, based on the same data and using a similar correction.

5.11. Ionization Energy and Electron Affinity of Cl. The value for the ionization energy of atomic chlorine, IE(Cl), is from Radziemski and Kaufman[126] (104591.0 ± 0.3 cm^{-1}; Moore[88] selects the same value).

The electron affinity of atomic chlorine, EA(Cl), is taken from Berry and Reimann[127] (3.613 ± 0.003 eV = 29141 ± 24 cm^{-1}), Trainham et al.[128] (29138.3 ± 0.5 cm^{-1}), and Berzinsh et al.[129] (29138.59 ± 0.22 cm^{-1}).

5.12. Calorimetric Studies of HCl. The enthalpy of combustion of hydrogen in chlorine, corresponding to the reaction $^1/_2\ H_2 + {}^1/_2\ Cl_2 \rightarrow HCl$, has been determined by Rossini[130]

(−92.312 ± 0.050 kJ/mol at 30 °C, corrected to current Joules and current molecular weight of HCl, 36.46064), Lacher et al.[131] (−22.233 ± 0.217 kcal/mol, at 248 °C, −93.02 ± 0.91 kJ/mol), and again by Lacher et al.[132] (−22.182 ± 0.15 kcal/mol at 100 °C, −92.81 ± 0.63 kJ/mol).

5.13. Ion-Pair Formation Threshold in HCl. The 0 K ion pair-formation threshold of HCl, IPF(HCl), corresponding to the reaction $HCl \rightarrow H^+ + Cl^-$, has been determined by Martin and Hepburn[133] (116289.1 ± 0.6 cm^{-1}, corrected here from ^{35}Cl to the average atomic weight of Cl of 35.4527 by standard isotopic relations, including the Y_{00} term, but neglecting possible electronic isotope shifts, i.e., non-Born-Oppenhaimer effects).

5.14. D_0(HCl$^+$). The bond dissociation energy in the positive ion of HCl, $D_0(HCl^+)$, has been determined by Michel et al.[134] (37537.0 ± 5 cm^{-1}) and again by Michel et al.[135] (37537.0 ± 0.5 cm^{-1}). Both determinations have been corrected from ^{35}Cl to the average atomic weight of Cl, as given above for the ion-pair formation threshold of HCl. The mass defect resulting from (1+) charge was neglected. The nominal isotope correction for IE(HCl) would be an additional increase by 0.04 cm^{-1}.

5.15. Photoionization and Photoelectron Studies of HCl. The 0 K appearance energy of the Cl^+ fragment from HCl, corresponding to the process $HCl \rightarrow H + Cl^+ + e^-$, has been determined by Krauss et al.[136] (17.34 ± 0.01 eV).

The ionization energy of HCl, IE(HCl), was taken from Natalis et al.[137] (12.747 ± 0.002 eV = 102811 ± 16 cm^{-1}), Tonkyn et al.[138] (102802.8 ± 2 cm^{-1}), and Drescher et al.[139] (102801.5 ± 1 cm^{-1}). In the latter two cases, the isotope shift corresponding to the average atomic weight of HCl has been considered.

5.16. D_0(F_2). The bond dissociation energy of F_2, $D_0(F_2)$, has been determined by Colburn et al.[140] (12920 ± 50 cm^{-1}). Unfortunately, no newer measurements of this crucial quantity are available.

5.17. Ionization Energy and Electron Affinity of F. The ionization energy of fluorine atom, IE(F), is from Liden[141] (140524.5 ± 0.4 cm^{-1}, Moore[88] recommends the same value).

The electron affinity of atomic fluorine, EA(F), has been determined by Berry and Reimann[127] (3.448 ± 0.005 eV) and Blondel et al.[142] (27432.440 ± 0.025 cm^{-1}).

5.18. Dissociative ionization and ion-pair formation threshold in F_2. The 0 K appearance energy of F^+ from F_2, AE(F^+/F_2), has been extracted from Dibeler et al.[143] (19.03 ± 0.05 eV) and from Berkowitz et al.[144,145] and Berkowitz and Wahl[146] (19.017 ± 0.016 eV).

The 0 K threshold for ion-pair formation in F_2, corresponding to $HF \rightarrow H^+ + F^-$, has been extracted from Berkowitz et al.[144,145] and Berkowitz and Wahl[146] (15.62 ± 0.01 eV).

The AE(F^+/F_2) threshold given by Dibeler et al.[143] is the first onset in the tail, rather than the thermochemically relevant threshold. An approximate graphical extrapolation of their data suggests 652−653 ± 2 Å = 19.00 ± 0.05 eV at 298 K, which, when corrected for the internal energy of 0.027 eV becomes 19.03 ± 0.05 eV at 0 K.

Berkowitz et al.[144] quote 19.008 eV for AE(F^+/F_2) at 0 K, a value repeated in a subsequent paper by the same group[145] and by Berkowitz and Wahl.[146] They also observe IPF(F_2). Berkowitz et al.,[145] in the discussion following the actual paper, quote the "linearly extrapolated" ion-pair formation threshold of 796.3 Å and point out that the difference between AE(F^+/F_2) − IPF(F_2) = 3.43 eV, approximately equal to the best then available EA(F) of 3.45 eV. However, the ion-pair formation threshold observed in photoionization experiments should be interpreted in a manner similar to parent ionization (e.g., through determining the mid-rise point), rather than through extrapolation to the baseline, which is the appropriate approach for dissociative ionization (fragment appearance) thresholds. In fact, in the related case of HF, the independently known ion-pair formation threshold seems to correspond to the mid-rise of the first autoionizing peak in the photoionization spectrum, i.e., lies even higher than the mid-rise of the assumed underlying step (and apparently corresponds to the turn-over point of the underlying step). A similar position in F_2 would correspond to approximately 794.0 ± 0.3 Å = 15.615 ± 0.006 eV, or perhaps more conservatively 15.62 ± 0.01 eV.

The value for AE(F^+/F_2) reported in Berkowitz et al.[144] was obtained by linear extrapolation. The onset sits on top of a broad feature identified as a higher energy re-appearance of the ion-pair process (verified by separately measuring F^-). Also, from their spectra and from the spectra in Dibeler et al.,[143] it is evident that the threshold has characteristic curvature toward higher energy, signifying that a linear extrapolation is likely to produce a threshold that is slightly too low. The modified value used in the TN has been obtained by re-interpretation of the spectra of Berkowitz et al.,[144] taking the effect of curvature into account. This reinterpretation suggests an onset of ~625.2 ± 0.5 Å = 19.010 ± 0.016 eV at 80 K, or 19.017 eV at 0 K.

5.19. D_0(HF). The bond dissociation energy of hydrogen fluoride, D_0(HF) is taken from Johns and Barrow[147] (47263 ± 100 cm^{-1}), Di Lonardo and Douglas[148] (47333 ± 60 cm^{-1}), and Zemke et al.[149,150] (47311 ± 5 cm^{-1}).

Note that Cox et al.[1] have implicitly selected $D_0(HF) = 47361 \pm 64$ cm^{-1}, based on routes that involve liquid and aqueous HF. Please also note that the current version of the TN contains thermochemistry relating to liquid and aqueous HF, but the determinations linking directly liquid and gaseous HF have been cut (by setting their external weights to zero), effectively locally decoupling the liquid/aqueous HF subgraph from the gaseous HF subgraph, since they appear to cause major inconsistencies affecting the value and uncertainty of the enthalpy of formation of liquid HF (but not affecting the results for gaseous HF). These links will be restored in future revisions of the TN, once the source of the inconsistency is thoroughly investigated and understood more clearly.

5.20. Dissociative Ionization in HF. The appearance energy of H^+ from HF, AE(H^+/HF), corresponding to $HF \rightarrow H^+ + F + e^-$, has been extracted from Berkowitz et al.[144,145] (19.454 ± 0.015 eV). The originally reported onset was linearly extrapolated from the photoionization spectrum. The value used here has been corrected for the curvature toward higher energy (similar to the case of F_2, see above).

5.21. Ion-Pair Formation Threshold in HF. The values for the 0 K threshold for the ion-pair formation in HF, IPF(HF), corresponding to $HF \rightarrow H^+ + F^-$, are from Hepburn[151] (129557.7 ± 1 cm^{-1}) and from a slight reinterpretation of the data of Yencha et al.[152] (16.0622 ± 0.0010 eV = 129550 ± 8 cm^{-1}).

5.22. Combustion Calorimetry on CO_2. As opposed to the combustion calorimetry of hydrogen (see above), there is a substantial number of determinations of the enthalpy of combustion of graphite to form CO_2. The determinations used in the Core TN have been recalculated from the original data of various authors and converted to standard enthalpies using additional correction terms (e.g., Hawtin et al.[153]), calibration improvements and discovery of errors and inaccuracies (e.g., Prosen et al.[154] or Rossini and Jessup[155]), and other details that were disclosed after the original determinations have been published. During these recalculations, we have found a number of cases where previous corrections were incomplete or inaccurate, even in papers attempting to correct errors in the original determinations, not to mention occasional typographical errors in the original works. The recalculated values were converted to current Joules and the current molecular weight of CO_2, 44.0095, atomic weight of C, 12.01070, or current values of the natural constants (depending on whether the amount of substance was determined from the weight of CO_2, weight of graphite, or volume of CO_2).

The determinations of the enthalpy of combustion of graphite (where, because of considerable variation in the properties of natural graphite samples, Acheson spectroscopic graphite is the currently accepted reference state for carbon, see Cox et al.[1]), corresponding to C (graphite) + $O_2 \rightarrow CO_2$, have been extracted from the data of Prosen and Rossini[156] (−393.560 ± 0.055 kJ/mol at 25 °C), Dewey and Harper[157] (−393.498 ± 0.062 kJ/mol at 25 °C), Jessup[158] (−393.447 ± 0.064 kJ/mol at 30 °C), Lewis et al.[159] (−393.462 ± 0.038 kJ/mol at 25 °C), Fraser and Prosen[160] (−393.468 ± 0.038 kJ/mol at 25 °C), Hawtin et al.[153] (−393.462 ± 0.056 kJ/mol and −393.464 ± 0.024 kJ/mol, both at 25 °C; the former is their direct new measurement, the latter is from considering all measurements that were available to them), and Prosen et al.[154] (−94.051 ± 0.011 kcal/mol at 25 °C = −393.509 ± 0.046 kJ/mol).

5.23. Combustion Calorimetry on CH_4. The values for the enthalpy of combustion of methane, corresponding to the reaction $CH_4 + 2\ O_2 \rightarrow CO_2 + 2\ H_2O$ (l), were obtained from a reanalysis of literature data. As in the case of CO_2, all determinations used in the TN were recalculated and/or rechecked from the original data. The determinations included in the Core TN were extracted from Roth and Banse[161] (−213.33 ± 0.50 kcal/mol at 20 °C = −892.6 ± 2.1 kJ/mol), Rossini[162,163,117] and Prosen and Rossini[164] (−889.849 ± 0.350 kJ/mol at 30 °C), and Pittam and Pilcher[165] (−890.699 ± 0.430 kJ/mol at 25 °C), as well as the newer determinations by Dale et al.[166] (−890.61 ± 0.21 kJ/mol at 25 °C) and by Alexandrov et al.[167,168] (−890.43 ± 0.35 kJ/mol at 25 °C).

5.24. Hydrogen/Methane/Graphite Equilibrium. The thermochemistry for the reaction $2\ H_2$ + C (graphite) $\rightarrow CH_4$ was extracted by reanalysis of the equilibrium study of Smith[169] (Gibbs energy of reaction of 37.521 ± 0.068 kJ/mol from 3rd Law analysis and enthalpy of reaction −88.55 ± 1.84 kJ/mol from 2nd Law analysis, both at 1165 K).

6. Illustrative Results and Discussion

Illustrative results for the enthalpies of formation of several simple chemical species, a fair number of which belong to "key" values (i.e., have been included in the CODATA compilation of Cox et al.[1]) are given in Table 1. The listed results are a subset of the solutions obtained from ATcT by solving the current version (1.033) of the Core TN, which contains approximately 250 species and 850 determinations. For comparison purposes, Table 1 also lists values from three popular reference thermochemical tables.[1−3]

The relevant determinations that define the secondary vertices of the initial TN are given in section 5 above. Starting from this initial TN, ATcT iteratively preconditioned the network using the "worst offender" procedure to resolve detected inconsistencies. When the procedure converged to a self-consistent state of the TN (approximately 400 iterations using an extra-fine step size), ATcT computed a simultaneous solution of the whole TN, producing the final enthalpies of formation and the associated uncertainties (all at the 95% confidence limit) that are sampled in Table 1. The quoted uncertainties have been independently verified in two additional manners. One involved a Monte Carlo analysis, the other the computation of sensitivity coefficients by numerical differentiation. The Monte Carlo analysis allows the computation of uncertainties by random sampling, and the sensitivity coefficients provide an alternate route to compute the covariance matrix from the initial uncertainties. Both checks reproduced the uncertainties computed by the direct algorithm given in the Appendix.

The manipulation of the TN by ATcT also required conversion of thermochemical information between 0 and 298.15 K (and in a few cases other temperatures). These were performed automatically as needed by ATcT, using the partition-function related information available in the ATcT libraries. For the subset of species reported here, the temperature dependence was calculated using direct counts for atoms and their ions, based on energy levels from NIST Database[34] and from Moore,[88] rigid-rotator-harmonic-oscillator estimates based on available spectroscopic data[170,171] combined with scaled[172] results of B3LYP/6-31G(d) calculations[173] for the ions of O_3, and tabular data from Cox et al.[1] and Gurvich et al.[3] for the other species.

It should be noted at this point that being able to make serious improvements to key thermochemical values is rather improbable or, at best, extremely difficult. This expectation applies to some extent to almost all the species in Table 1 but is particularly true for the species given in the CODATA compilation of Cox et al.[1] One reason for this is that the goal of the CODATA evaluation was to exercise a particularly stringent critical analysis for a select small group of species that lie at the foundation of thermochemistry, and hence produce a compilation of "definitive" thermochemical values. Another reason emanates from the fundamental nature of these species, which means that their enthalpies of formation have been used very frequently over the last several decades and hence implicitly tested, retested, and validated. Finally, because these species are at the foundation of thermochemistry, the pedigree that connects them to the elements in reference states is relatively simple, which implies that these species are not likely to suffer from errors propagated from earlier steps in the sequential process that was used in traditional compilations.

Nevertheless, the ATcT values show improvements for most species in Table 1. In almost all cases, the enhancement in the uncertainty is significant and in some cases even spectacular. In several cases, the new enthalpies of formation are outside the uncertainty limits of previously recommended values. The improvement in the values and uncertainties of the listed enthalpies of formation is a synergistic effect resulting from the inclusion of new data, the utilization of a variety of competing measurements, and the availability of alternative pathways through the TN.

A good example of the synergistic effect obtained from the ATcT approach is the new value for the enthalpy of formation of O_3. The older data[67−69] on the equilibrium $^3/_2\ O_2 \rightarrow O_3$ were utilized by Gurvich et al.[3] and lead to $\Delta_f H^\circ_{298}(O_3) = 141.8 \pm 2.0$ kJ/mol. JANAF[2] utilized a subset of the older data (and interpreted it somewhat differently than Gurvich et al.[3]) and recommended a higher value $\Delta_f H^\circ_{298}(O_3) = 142.67_4 \pm 1.7$ kJ/mol. The new data by Takahashi et al.[70] and Taniguchi et al.[71] have been used by the latter authors to propose the improved value $\Delta_f H^\circ_0(O_3) = 144.31 \pm 0.14$ kJ/mol, which translates to 141.66 ± 0.14 kJ/mol at 298.15 K (note that Taniguchi et al. have accidentally switched the sign of the enthalpy of formation). The value of Taniguchi et al. reflects the consequences of the new determinations through conventional sequential thermochemistry. The ATcT value, which utilizes both the

TABLE 1: ATcT Values and Uncertainties (Corresponding to 95% Confidence Limits) for the Enthalpies of Formation of Several Key Chemical Species, Compared with the Existing Values from Three Popular Thermochemical Compilations

	CODATA[b]		JANAF[c]		Gurvich et al.[d]		ATcT[e]	
species[a]	298.15 K	0 K	298.15 K	0 K	298.15 K	0 K	298.15 K	0 K
O	249.18	*246.79_5*	249.173	246.790	249.18	246.79_5	**249.229_2**	**246.844**
	±0.10		±0.10		±0.10		**$\pm 0.002_0$**	
O^+			1562.588^f	1560.733	1562.595^f	1560.738	**1562.643_7**	**1560.786**
			±0.10		±0.10		**$\pm 0.002_1$**	
O^-			108.043^f	105.814	107.826^f	105.595	**108.097_1**	**105.868**
			± ?		±0.61		**$\pm 0.002_0$**	
O_2^+			1164.6_{91}^f	1164.7	1165.6_{31}^f	1165.0	**1165.210**	**1164.579**
			±0.8		±0.4		**±0.013**	
O_2^-			-42.39_5^f	-42.46_4	-41.8_{56}^f	−42.5	**−42.370**	**−43.014**
			±0.75		±0.8		**±0.52**	
O_3			142.674	145.348	141.8	144.4_{54}	**141.732**	**144.386**
			±1.7		±2.0		**±0.039**	
O_3^+							**1349.94**	**1352.55**
							±0.33	
O_3^-							**−60.85**	**−58.50**
							±0.20	
H	217.998	*216.035*	217.999	216.035	217.998	216.035	**217.997_{81}**	**216.034**
	±0.006		±0.006		±0.006		**$\pm 0.000_{10}$**	
H^+			1530.048^f	1528.085	1530.047^f	1528.084	**1530.047_{31}**	**1528.084**
			±0.04		±0.006		**$\pm 0.000_{10}$**	
H^-			145.229^f	143.266	145.228^f	143.265	**145.227_{92}**	**143.264**
			±0.02		±0.006		**$\pm 0.000_{15}$**	
H_2^+			1488.474^f	1488.358	1488.475^f	1488.360	**1488.479_{58}**	**1488.364**
			±0.004		±0.005		**$\pm 0.000_{16}$**	
D			221.720	219.807	221.720	219.808	**221.716_{84}**	**219.804**
			±0.004		±0.003		**$\pm 0.000_{03}$**	
D^+			1534.12_7^f	1532.21_4			**1534.123_{33}**	**1532.210**
			±0.04				**$\pm 0.000_{03}$**	
D^-			148.950^f	147.038			**148.908**	**146.995**
			±0.04				**±0.006**	
HD			0.321	0.330	0.323	0.332	**0.319_{05}**	**0.328**
			±0.008		±0.008		**$\pm 0.000_{16}$**	
HD^+			1490.596^f	1490.499			**1490.587_{15}**	**1490.498**
			±0.021				**$\pm 0.000_{20}$**	
H_2O (cr,l)	−285.830	*−286.295*	−285.830	-	−285.830	−286.295	**−285.823**	**−286.289**
	±0.040		±0.042				**±0.033**	
H_2O	−241.826	*−238.923*	−241.826	−238.921	−241.826	−238.923	**−241.818**	**−238.916**
	±0.040		±0.042		±0.040		**±0.033**	
H_2O^+					975.403^f	978.277	**975.673**	**978.546**
					±0.5		**±0.039**	
F	79.38	*77.27_4*	79.39	77.28_4	79.38	77.27_5	**79.313**	**77.207**
	±0.30		±0.30		±0.30		**±0.24**	
F^+			1760.62_9^f	1758.33_1			**1760.551**	**1758.253**
			±0.3				**±0.24**	
F^-			-248.88_2^f	-250.66_7	-248.951^f	−250.735	**−249.173**	**−250.958**
			±0.6		±0.35		**±0.24**	
HF	−273.30	*-273.25_2*	−272.546	−272.499	−273.30	-273.25_2	**−272.775**	**−272.728**
	±0.70		±0.8		±0.70		**±0.24**	
Cl	121.301	*119.620*	121.302	119.621	121.302	119.620	**121.302_6**	**119.622**
	±0.008		±0.008		±0.008		**$\pm 0.001_7$**	
Cl^+			1372.604^f	1370.807			**1372.602_9**	**1370.807**
			±0.01				**$\pm 0.003_8$**	
Cl-			-227.757^f	−229.36	-227.47_4^f	−229.08	**-227.345_5**	**−228.952**
			±0.4		±0.20		**$\pm 0.002_9$**	
HCl	−92.31	*-92.12_6*	−92.312	−92.127	−92.31	-92.12_5	**-92.176_3**	**−91.992**
	±0.10		±0.21		±0.10		**$\pm 0.006_6$**	
HCl^+							**1137.613_3**	**1137.797**
							$\pm 0.006_3$	
CO_2	−393.51	*-393.14_5*	−393.522	−393.151	−393.51	-393.14_5	**−393.473**	**−393.107**
	±0.13		±0.05		±0.13		**±0.014**	
CH_4			−74.873	−66.911	−74.60	-66.63_0	**−74.549**	**−66.580**
			±0.34		±0.30		**±0.060**	

[a] All species are in gaseous state, except for H_2O (cr, l), which refers to the condensed state. [b] Reference 1; Cox et al. do not provide explicitly the 0 K values (listed here in italics), but these can be trivially computed using the enthalpy increments given in that reference. [c] Reference 2. [d] Reference 3. [e] Values obtained from the Core (Argonne) Thermochemical Network contained in MainLibrary ver. 1.033 using Active Thermochemical Tables ver. 1.25. [f] Though JANAF[2] and Gurvich et al.[3] use the thermal electron convention, the values for ions have been converted here to the stationary electron convention, which was adopted in this paper. The 298.15 K enthalpies of formation of ions can be converted back to the thermal electron convention by adding (for positive ions) or subtracting (for negative ions) 6.197 kJ/mol. The values at 0 K for ions (and at both temperatures for neutral species) is the same in both conventions.

newer and the older data, together with all the other information available in the TN, is $\Delta_f H^\circ_{298}(O_3) = 141.732 \pm 0.039$ kJ/mol.

The ATcT value for $\Delta_f H^\circ(O)$ shows a rather spectacular improvement. The uncertainty has now dropped from the CODATA[1] value of ±0.10 kJ/mol to $\pm 0.002_0$ kJ/mol. In addition, the new value is slightly larger. Both effects are greatly influenced by the inclusion of new measurements of $D_0(O_2)$ and of the ion-pair formation threshold of O_2. Although interesting from the academic viewpoint more than from a practical viewpoint, $\Delta_f H^\circ(H)$ also shows a significant improvement in the uncertainty, which has now dropped from 0.006 kJ/mol to $\pm 0.000_1$ kJ/mol. Similarly, the uncertainty of $\Delta_f H^\circ$(D) has dropped from ±0.003 kJ/mol to $\pm 0.000_{03}$ kJ/mol. In the latter case, there is also a minor change in the value of the enthalpy of formation. The improvements in the uncertainties of the enthalpies of formation of O, H, and D propagate further to the enthalpies of their positive and negative ions, as well as to the enthalpy of formation of HD.

The uncertainty in $\Delta_f H^\circ(Cl)$ has also improved by a significant factor. On the other hand, the improvement in $\Delta_f H^\circ(F)$ is quite modest. The TN clearly indicates that the bottleneck is created by a relatively high uncertainty in the existing determination of $D_0(F_2)$ and the lack of alternate network pathways that would have comparable or better accuracy. What is highly desired here are new and accurate measurements of one (or more) of the following quantities: $D_0(F_2)$, IPF(F_2), or AE(F^+/F_2).

Another rather spectacular improvement is in $\Delta_f H^\circ(HCl)$, where the uncertainty dropped from ±0.10 kJ/mol to $\pm 0.006_6$ kJ/mol, and the new value is just outside the uncertainty of the CODATA[1] value. Again, the improvement is strongly influenced by newer measurements and by the underlying improvements in the enthalpies of the constituent atoms and their ions.

The enthalpy of formation of gaseous HF, $\Delta_f H^\circ(HF)$, has a long history replete with controversies arising from the fact that different (and inconsistent) results were obtained from pathways relating to gaseous HF directly (spectroscopic studies) and pathways relating to gaseous HF via condensed phase and/or aqueous HF (calorimetric studies). To state the history succinctly, the recommended value in various compilations depended on which pathway was favored by the evaluator. The appearance of the CODATA value seemed to have put an end to the controversy or, at least, the alternate pathways appeared to be consistent within the associated uncertainty of $\Delta_f H^\circ(HF)$. The new determinations of $D_0(HF)$ and IPF(HF) are effectively reviving the old controversy. Namely, the new measurements produce significant improvements to the thermochemistry of gaseous HF, and the tightened uncertainty cannot accommodate a compromise any more. Furthermore, the situation has now changed in favor of the gas-phase pathways, strongly indicating that the source of discrepancy is most likely somewhere in the domain of condensed phase and/or aqueous HF, and/or in determinations linking those domains to the gas phase. It should be also noted that the accuracy of the current ATcT value for $\Delta_f H^\circ(HF)$ is, in fact, limited by the underlying uncertainty in $\Delta_f H^\circ(F)$. The new value for the enthalpy of formation of HF differs significantly from the CODATA[1] value (albeit is still within the range of its large uncertainty). The JANAF[2] value was adopted before the CODATA value was made public and never updated and was believed to be wrong practically since the appearance of the 3rd edition of JANAF tables. The irony of the situation is that the “wrong” JANAF value is, in fact, much closer to the new value than the generally accepted CODATA value.

The new enthalpy of formation of H_2O (both liquid and gas phase) is insignificantly different than the CODATA[1] value. The primary reasons are that the relevant determinations link liquid water directly to the elements in their reference states, that there are only two competing measurements of any significance (and one of them is much more accurate than the other) and that the critical reevaluation of these two determinations has simply confirmed the prior interpretations. Similarly, gaseous water is removed only by one additional step, involving the enthalpy of vaporization, which also has not changed.

On the other hand, $\Delta_f H^\circ(CO_2)$, where one would have expected a situation not dissimilar to the one encountered in water, displays a rather remarkable improvement in the uncertainty, The improvement appears to be due to a synergistic confluence of at least two factors. The first factor is that the underlying measurements have been thoroughly reevaluated in the course of preparing the current TN, apparently creating a new set of initial values that appears to be slightly more congruent than the equivalent sets emerging from previous critical evaluations. A second factor is that the statistical improvement, which is inherently expected when concordant measurements are considered together, as opposed to selecting only one “best” measurement, tends to became more obvious as the number of such measurements increases. The improvement in the enthalpy of formation of CH_4 is due to a confluence of even more factors. Some of the improvement can be traced to effects analogous to those present in the case of CO_2, further leveraged by the introduction of two new determinations. An additional important factor in the improvement of $\Delta_f H^\circ(CH_4)$ comes from the propagation of the underlying improvement in the enthalpy of formation of CO_2.

7. Conclusion

The concept behind active thermochemical tables, a new paradigm of how to derive accurate, reliable, and internally consistent thermochemistry, has been presented. The ATcT approach addresses the principal disadvantages present in traditional sequential thermochemistry. The sequential approach is based on a stepwise procedure, which utilizes the existing knowledge only partially, and produces a compilation that contains a maze of hidden progenitor−progeny dependences. The latter aspect frustrates any attempts to properly update a traditional thermochemical table with new knowledge.

As opposed to traditional sequential thermochemistry, ATcT utilizes the thermochemical network approach. The TN is defined by the underlying set of thermochemically relevant determinations, and the desired thermochemical properties of individual species, such as enthalpies of formation, are obtained by considering all of the knowledge that is present in the TN. This process involves, inter alia, a statistical analysis of the TN. The analysis helps identify determinations that have “optimistic” uncertainties and would, if left uncorrected, tend to distort the final result. The evaluation of self-consistency of the TN is made possible by redundancies in the TN, such as competing measurements and alternate network pathways that interrelate the various chemical species. The desired thermochemical values are obtained by simultaneous solution of the self-consistent TN in error-weighted space, making optimal use of all the knowledge present in the TN.

ATcT also has a number of additional novel features that are not present nor possible in the traditional approach. The resulting thermochemistry can be updated painlessly with new knowledge, which immediately propagates through all affected thermochemical values. ATcT also allows hypothesis testing and evaluation, as well as discovery of weak links in the TN.

The latter aspect provides pointers to new experimental or theoretical determinations that will most efficiently improve the underlying thermochemical body of knowledge.

The ATcT approach is briefly illustrated by providing improved thermochemistry for several key thermochemical species. Though the thermochemistry of virtually all off the species presented in this introductory paper has been generally considered to be already well established in traditional thermochemical tabulations (except perhaps ozone and its ions), ATcT has nevertheless produced additional improvements. In almost all cases, the enhancement in the uncertainty is significant and, in some cases, even spectacular. Several new enthalpies of formation are outside the uncertainty limits of previously recommended values. The improvement in the values and uncertainties of the listed enthalpies of formation is a synergistic effect, resulting from the inclusion of new data, the utilization of a variety of competing measurements, and the availability of alternative pathways through the TN.

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Appendix

A TN consists of *n* determinations, such as enthalpies of reaction, $\Delta_r H^\circ_T$, Gibbs energies of reaction, $\Delta_r G^\circ_T$, equilibrium constants, $K_{eq,T}$, etc., involving *m* thermochemically distinct chemical species. Let some *i*th determination correspond to the chemical equation

$$k_{Ai}A + k_{Bi}B \rightarrow k_{Ci}C + k_{Di}D$$

for which a relevant thermochemical quantity, such as $\Delta_r H^\circ_T(i)$, $\Delta_r G^\circ_T(i)$, or $K_{eq,T}(i)$, has been determined. Here A, B, C, and D are the chemical species involved, and k_{Ai}, k_{Bi}, etc. are their stoichiometric factors.

The chemical equation that is given above maps onto a subgraph of the associated mathematical graph of the TN. The subgraph contains four primary vertices, A, B, C, and D, and one secondary vertex *i*. One directed edge connects each of the primary vertices to the secondary vertex. The edges connecting A and B (reactants) to the secondary vertex point toward *i*, and the edges connecting C and D (products) point away from *i*. The weights of the four edges are k_{Ai}, k_{Bi}, k_{Ci}, and k_{Di}, respectively.

By using the appropriate partition functions for the species involved, all measured quantities $\Delta_r H^\circ_T(i)$, $\Delta_r G^\circ_T(i)$, $K_{eq,T}$, ... that are selected to create the TN can be conveniently transformed into one and the same type of quantity at one and the same selected temperature *T* for the whole Network. Let us assume that all initial quantities are transformed into standard reaction enthalpies at 298.15 K

$$\Delta_r H^\circ_{298}(i) = Y_i \pm Z_i$$

where Y_i is the transformed value of the original determination *i*, such that it corresponds to an enthalpy of reaction at 298.15 K, and Z_i is the associated uncertainty as given by the original authors and/or modified by the evaluator to closely reflect some uniform confidence limit that was selected as the standard across the whole TN (for example, the 95% confidence limit). Here it is assumed that, as part of the evaluation of the initial data selected to create the TN, all Z_i were made to correspond approximately to the same confidence limit. (In ATcT, the initial data are, in fact, given as the originally measured quantity in the originally reported units and at the original measurement temperature, and the meaning of the uncertainty, if different than the default 95% confidence limit, is specified; ATcT then takes care of the transformation into the common type of quantity, common temperature, and common coverage factor for the uncertainty.)

Each determination corresponds to a linear equation, producing a system of *n* equations with *m* unknowns

$$f_i(\Delta H_A,\Delta H_B,\Delta H_C,...,\Delta H_m;S_{Ai},S_{Bi},S_{Ci},...,S_{mi}) = Y_i \pm Z_i \; i = 1,2,...,n$$

where for the *i*th determination the function f_i is

$$f_i(\Delta H_A,\Delta H_B,\Delta H_C,...,\Delta H_m;S_{Ai},S_{Bi},S_{Ci},...,S_{mi}) = S_{Ai}\Delta H_A + S_{Bi}\Delta H_B + S_{Ci}\Delta H_C + ... + S_{mi}\Delta H_m$$

The symbols such as ΔH_A are a shorthand for $\Delta_f H^\circ_{298}(A)$, the standard enthalpy of formation of species A at 298.15 K, and correspond to the unknowns that will be optimized by solving the system. S_{Ai} is the stoichiometric factor k_{Ai} with the proper algebraic sign ($S_{Ai} = -k_{Ai}$ if A is a reactant, and $S_{Ai} = k_{Ai}$ if A is a product in the chemical reaction of the *i*th determination). S_{Ai} is obviously zero if species A does not participate in the corresponding chemical reaction. The system is overdetermined if $n > m$, exact if $n = m$, and underdetermined (intractable) if $n < m$. The system can also be intractable if the TN is "floating", i.e., has insufficient references to elements in their reference states or, in case of a local TN, an inappropriate selection of fixed primary vertices.

In matrix format, the system of equations can be expressed as

$$\mathbf{SH} = \mathbf{Y}$$

where

$$\mathbf{S} = \begin{pmatrix} S_{A1} & S_{B1} & S_{B1} & ... & S_{m1} \\ S_{A2} & S_{B2} & S_{C2} & ... & S_{m2} \\ S_{A3} & S_{B3} & S_{C3} & ... & S_{m3} \\ ... & ... & ... & ... & ... \\ S_{An} & S_{Bn} & S_{Cn} & ... & S_{mn} \end{pmatrix}$$

$$\mathbf{H} = \begin{pmatrix} \Delta H_A \\ \Delta H_B \\ \Delta H_C \\ ... \\ \Delta H_m \end{pmatrix}$$

$$\mathbf{Y} = \begin{pmatrix} Y_1 \pm Z_1 \\ Y_2 \pm Z_2 \\ Y_3 \pm Z_3 \\ ... \\ Y_n \pm Z_n \end{pmatrix}$$

S has *n* rows and *m* columns, and the column-vectors **H** and **Y** have *m* and *n* elements, respectively. Note that **S** relates to the adjacency matrix of the associated mathematical graph of the TN.

In case of a global TN, the columns of **S** that refer to elements in their reference states can be simply removed, together with the related elements of **H**. In case of a local TN, the columns of **S** referring to the primary vertices that are held fixed can be eliminated by modifying appropriately the vector **Y**. For a fixed vertex *k*, whose "solution" is held at some value ΔH_k, the modification of **Y** means adding the quantity $-S_{ki}\Delta H_k$ to all Y_i and propagating appropriately the uncertainty of ΔH_k to Z_i.

Let us now assume that the evaluator has done a decent job during the initial selection of data, and selected/evaluated the associated uncertainties in such a way that they fairly represent the underlying probability of getting the value Y_i as an outcome of a determination of the reaction enthalpy for the underlying chemical reaction $k_{Ai}A + k_{Bi}B \rightarrow k_{Ci}C + k_{Di}D$, and that, therefore, each Z_i corresponds to $t_i\sigma_i$, where σ_i is the standard deviation of determination *i*. The multiplicative factor t_i is in general interpreted through the appropriate Student-*t* distribution, taking into account the desired confidence level and the size of the sample on which Y_i is based. In the limit of a large sample, if $t_i = 1$, then Z_i will represent ~68% confidence limit, if $t_i = 2$ then Z_i will represent ~95% confidence limits, etc. Let us also assume that the evaluator has selected or adjusted the Z_i in such a way that the factors t_i are, at least to a first approximation, uniform for all determinations involved in the TN, i.e.

$$t_1 \approx t_2 \approx t_3 \approx ... \approx t_i = t$$

Let us further make the assumption that the likelihoods of obtaining Y_i as the outcome of the corresponding determinations are fairly described via normal distributions (either because the particular determination is indeed subject to statistical scatter that has properties close to a normal distribution, or because the evaluator has manipulated the associated Z_i in such a way that the probability of getting Y_i is fairly described by the equivalent normal distribution implied in the value of Z_i). Then, the total probability P_{TN} of getting the existing set of *n* measurements that define the TN within some small interval of values δY is

$$P_{TN} \propto \prod_{i=1}^{n} \delta Y e^{-1/2\{[f_i(\Delta H_A,\Delta H_B,\Delta H_C,...,\Delta H_m;S_{Ai},S_{Bi},S_{Ci},...,S_{mi})-Y_i]/\sigma_i\}^2} = \delta Y^n e^{-1/2\chi^2}$$

where χ^2 is the usual chi-square

$$\chi^2 = \sum_{i=1}^{n}\left[\frac{f_i(\Delta H_A,\Delta H_B,\Delta H_C,...,\Delta H_m;S_{Ai},S_{Bi},S_{Ci},...,S_{mi}) - Y_i}{\sigma_i}\right]^2 = t^2\sum_{i=1}^{n} \times \left[\frac{f_i(\Delta H_A,\Delta H_B,\Delta H_C,...,\Delta H_m;S_{Ai},S_{Bi},S_{Ci},...,S_{mi}) - Y_i}{Z_i}\right]^2$$

Maximizing P_{TN} is equivalent to minimizing χ^2.

To proceed with obtaining the optimized set of ΔH_A, ΔH_B, ΔH_C, ..., ΔH_m that minimizes χ^2, it is very convenient to linearly weigh each equation *i* by the reciprocal of the associated uncertainty Z_i. This transformation leads to a space where all measurements have unit uncertainty or a $1/t^2$ variance. The system of equations now becomes

$$f_i(\Delta H_A,\Delta H_B,\Delta H_C,...,\Delta H_m;s_{Ai},s_{Bi},s_{Ci},...,s_{mi}) = y_i \pm 1 \qquad i = 1,2,...,n$$

$$f_i(\Delta H_A,\Delta H_B,\Delta H_C,...,\Delta H_m;s_{Ai},s_{Bi},s_{Ci},...,s_{mi}) = s_{Ai}\Delta H_A + s_{Bi}\Delta H_B + s_{Ci}\Delta H_C + ... + s_{mi}\Delta H_m$$

where

$$y_i = \frac{Y_i}{Z_i};\ s_{Ai} = \frac{S_{Ai}}{Z_i},\ s_{Bi} = \frac{S_{Bi}}{Z_i},\ s_{Ci} = \frac{S_{Ci}}{Z_i},\ ...,\ s_{mi} = \frac{S_{mi}}{Z_i}$$

or, in matrix form

$$\mathbf{sH} = \mathbf{y}$$

where

$$\mathbf{s} = \begin{pmatrix} s_{A1} & s_{B1} & s_{C1} & ... & s_{m1} \\ s_{A2} & s_{B2} & s_{C2} & ... & s_{m2} \\ s_{A3} & s_{B3} & s_{C3} & ... & s_{m3} \\ ... & ... & ... & ... & ... \\ s_{An} & s_{Bn} & s_{Cn} & ... & s_{mn} \end{pmatrix}$$

$$\mathbf{H} = \begin{pmatrix} \Delta H_A \\ \Delta H_B \\ \Delta H_C \\ ... \\ \Delta H_m \end{pmatrix}$$

$$\mathbf{y} = \begin{pmatrix} y_1 \pm 1 \\ y_2 \pm 1 \\ y_3 \pm 1 \\ ... \\ y_n \pm 1 \end{pmatrix}$$

with **s** being the design matrix of the optimization problem. χ^2 now has the form

$$\chi^2 = t^2\sum_{i=1}^{n}[f_i(\Delta H_A,\Delta H_B,\Delta H_C,...,\Delta H_m;s_{Ai},s_{Bi},s_{Ci},...,s_{mi}) - y_i]^2$$

Minimizing over the parameters ΔH_A, ΔH_B, ΔH_C, ..., ΔH_m leads to *m* conditions of the type

$$\frac{\partial}{\partial \Delta H_A} \times \sum_{i=1}^{n}[f_i(\Delta H_A,\Delta H_B,\Delta H_C,...,\Delta H_m;s_{Ai},s_{Bi},s_{Ci},...,s_{mi}) - y_i]^2 = 0$$

that trivially evolve into equations of the type

$$\sum_{i=1}^{n} s_{Ai}{}^2\Delta H_A + \sum_{i=1}^{n} s_{Ai}s_{Bi}\Delta H_B + \sum_{i=1}^{n} s_{Ai}s_{Ci}\Delta H_C + ... + \sum_{i=1}^{n} s_{Ai}s_{mi}\Delta H_m = \sum_{i=1}^{n} s_{Ai}y_i$$

corresponding to an exact system of *m* linear equations with *m* unknowns, i.e., producing the normal equations of the least-squares problem

$$\mathbf{aH} = \mathbf{w}$$

where

$$\mathbf{a} = \mathbf{s}^{\mathrm{T}}\mathbf{s} = \begin{pmatrix} \sum_{i=1}^{n} s_{\mathrm{A}i}^{2} & \sum_{i=1}^{n} s_{\mathrm{A}i}s_{\mathrm{B}i} & \sum_{i=1}^{n} s_{\mathrm{A}i}s_{\mathrm{C}i} & \cdots & \sum_{i=1}^{n} s_{\mathrm{A}i}s_{mi} \\ \sum_{i=1}^{n} s_{\mathrm{A}i}s_{\mathrm{B}i} & \sum_{i=1}^{n} s_{\mathrm{B}i}^{2} & \sum_{i=1}^{n} s_{\mathrm{B}i}s_{\mathrm{C}i} & \cdots & \sum_{i=1}^{n} s_{\mathrm{B}i}s_{mi} \\ \sum_{i=1}^{n} s_{\mathrm{A}i}s_{\mathrm{C}i} & \sum_{i=1}^{n} s_{\mathrm{B}i}s_{\mathrm{C}i} & \sum_{i=1}^{n} s_{\mathrm{C}i}^{2} & \cdots & \sum_{i=1}^{n} s_{\mathrm{C}i}s_{mi} \\ \cdots & \cdots & \cdots & \cdots & \cdots \\ \sum_{i=1}^{n} s_{\mathrm{A}i}s_{mi} & \sum_{i=1}^{n} s_{\mathrm{B}i}s_{mi} & \sum_{i=1}^{n} s_{\mathrm{C}i}s_{mi} & \cdots & \sum_{i=1}^{n} s_{mi}^{2} \end{pmatrix}$$

$$\mathbf{H} = \begin{pmatrix} \Delta H_{\mathrm{A}} \\ \Delta H_{\mathrm{B}} \\ \Delta H_{\mathrm{C}} \\ \cdots \\ \Delta H_{m} \end{pmatrix}$$

$$\mathbf{w} = \mathbf{s}^{\mathrm{T}}\mathbf{y} = \begin{pmatrix} \sum_{i=1}^{n} s_{\mathrm{A}i}y_i \\ \sum_{i=1}^{n} s_{\mathrm{B}i}y_i \\ \sum_{i=1}^{n} s_{\mathrm{C}i}y_i \\ \cdots \\ \sum_{i=1}^{n} s_{mi}y_i \end{pmatrix}$$

If det|**a**| $\neq 0$, then the system can be solved via

$$\mathbf{H} = \mathbf{cw},\ \mathbf{c} = \mathbf{a}^{-1}$$

where **c** is the covariance matrix of the system. (If det|**a**| $= 0$, the system is intractable, e.g., corresponds to a "floating" TN.)

The standard deviation of the fitted enthalpies of formation ΔH_{A}, ΔH_{B}, ΔH_{C}, ..., ΔH_m can be obtained from

$$\sigma_j^{2} = \sum_{i=1}^{n} \sigma_i^{2}\left(\frac{\partial}{\partial Y_i}\Delta H_j\right)^{2}, \qquad j = \mathrm{A,B,...,}m$$

Since

$$y_i = \frac{Y_i}{Z_i} = \frac{Y_i}{t\sigma_i}$$

and

$$\partial Y_i = t\sigma_i \partial y_i$$

then

$$\sigma_j^{2} = \frac{1}{t^{2}}\sum_{i=1}^{n}\left(\frac{\partial}{\partial y_i}\Delta H_j\right)^{2}, \qquad j = \mathrm{A,B,...,}m$$

Note that since $\mathbf{H} = \mathbf{a}^{-1}\mathbf{w} = \mathbf{cw}$, i.e., since the solutions ΔH_j, j = A, B, ..., m are obtained from

$$\Delta H_j = \sum_{k=1}^{m} \mathbf{a}_{jk}{}^{-1}\mathbf{w}_k = \sum_{k=1}^{m} \mathbf{c}_{jk}\Big[\sum_{i=1}^{n} s_{ki}y_i\Big] = \frac{1}{t^{2}}\sum_{k=1}^{m} \mathbf{c}_{jk}\left[\sum_{i=1}^{n} \frac{S_{ki}Y_i}{\sigma_i^{2}}\right]$$

and since **a** (and hence **c**) is independent of Y_i

$$\frac{\partial}{\partial y_i}\Delta H_j = \sum_{k=1}^{m} \mathbf{c}_{jk}s_{ki}$$

or

$$\frac{\partial}{\partial Y_i}\Delta H_j = \frac{1}{t^{2}}\sum_{k=1}^{m} \mathbf{c}_{jk}\frac{S_{ki}}{\sigma_i^{2}}$$

then

$$\sigma_j^{2} = \frac{1}{t^{4}}\sum_{k=1}^{m}\sum_{l=1}^{m} \mathbf{c}_{jk}\mathbf{c}_{jl}\left[\sum_{i=1}^{n}\frac{S_{ki}S_{il}}{\sigma_i^{2}}\right] = \frac{1}{t^{2}}\sum_{k=1}^{m}\sum_{l=1}^{m} \mathbf{c}_{jk}\mathbf{c}_{jl}\Big[\sum_{i=1}^{n} s_{ki}s_{il}\Big]$$

Noting that

$$\mathbf{a}_{kl} = \sum_{i=1}^{n} s_{ki}s_{il}$$

and that

$$\mathbf{ca} = \mathbf{1}$$

then

$$\sigma_j^{2} = \frac{1}{t^{2}}\sum_{k=1}^{m}\sum_{l=1}^{m} \mathbf{c}_{jk}\mathbf{c}_{jl}\mathbf{a}_{jl} = \frac{1}{t^{2}}\mathbf{c}_{jj}$$

or, the variances of the fitted parameters ΔH_{A}, ΔH_{B}, ΔH_{C},..., ΔH_m are given by the diagonal elements of the covariance matrix scaled by $1/t^2$. Conversely

$$\mathbf{c}_{jj} = t^{2}\sigma_j^{2}$$

i.e., the square roots of the diagonal elements correspond directly to uncertainties of the solutions ΔH_j that have the meaning of $t\ \sigma_j$, congruent in terms of confidence limits to the initial uncertainties Z_i.

At this point, we would like to clarify some persistent confusion that seems to exist with respect to the question of linear vs quadratic weighting of the system of linear equations. Garvin et al.,[17] for example, remark that the common weighting procedure in a least-squares analysis is to use weights proportional to the square of the reciprocal of the uncertainty, but they advocate (and use) linear weights, pointing out that quadratic weights would favor too strongly a few selected measurements. We entirely agree with the assessment that quadratic weighting would give a disproportionate emphasis to a few selected determinations, but we disagree that the choice is subject to an arbitrary matter of opinion. Namely, we have shown above why minimizing χ^2 appears to be a natural choice. Minimizing χ^2 implies linear weighting of the equations. Perhaps the quadratic weighting alluded to by Garvin et al.[17] is the approach commonly applied when computing a weighted average of some quantity. It can be readily shown that, in the trivial limit of an overdetermined system of equations involving only one unknown, linear weighting of the initial equations leads to a solution that corresponds to a quadratically weighted average.

Let us suppose that some quantity Q has been measured n times, resulting in measurements $Y_i \pm Z_i$, $i = 1, 2, ..., n$, where the uncertainties Z_i are related to the standard deviations σ_i of each measurement via some common factor t. These can be represented via an overdetermined set of n equations

$$Q = Y_i \pm Z_i, i = 1, 2, ..., n$$

Then, after linear weighting of the above equations

$$\mathbf{s} = \begin{pmatrix} 1/Z_1 \\ 1/Z_2 \\ 1/Z_3 \\ ... \\ 1/Z_n \end{pmatrix}, \mathbf{H} = Q, \text{ and } \mathbf{y} = \begin{pmatrix} Y_1/Z_1 \pm 1 \\ Y_2/Z_2 \pm 1 \\ Y_3/Z_3 \pm 1 \\ ... \\ Y_n/Z_n \pm 1 \end{pmatrix}$$

resulting in

$$\mathbf{a} = \mathbf{s}^{\mathrm{T}}\mathbf{s} = \sum_{i=1}^{n} 1/Z_i^2$$

$$\mathbf{w} = \mathbf{s}^{\mathrm{T}}\mathbf{y} = \sum_{i=1}^{n} y_i/Z_i = \sum_{i=1}^{n} Y_i/Z_i^2$$

and

$$Q = \mathbf{a}^{-1}\mathbf{w} = \frac{\sum_{i=1}^{n} Y_i/Z_i^2}{\sum_{i=1}^{n} 1/Z_i^2}$$

which is the traditional quadratically weighted average of a set of determinations of some quantity Q. Therefore, the more general approach of weighting an overdetermined set of linear equations by the reciprocal of the uncertainties is entirely equivalent to the approach of finding the quadratically weighted average for the case of a single unknown.

Note also that in the above case of a single unknown the covariance matrix is simply

$$\mathbf{c} = \mathbf{a}^{-1} = \sum_{i=1}^{n} 1/Z_i^2$$

and hence the uncertainty $\pm q$ of the averaged value of Q is given by

$$q = t\sigma_Q = \sqrt{\sum_{i=1}^{n} 1/Z_i^2}$$

Returning to the case of n determinations of m unknowns, let us remark on another commonly used alternative measure of the goodness of the fit: the standard deviation of the overall fit, σ_{fit}, given by

$$\sigma_{\mathrm{fit}}^2 = \frac{\chi^2}{n - m} = t^2 \frac{\sum_{i=1}^{n} [y_i - f(\Delta H_{\mathrm{A}},\Delta H_{\mathrm{B}},\Delta H_{\mathrm{C}},...,\Delta H_m;s_{\mathrm{A}i},s_{\mathrm{B}i},s_{\mathrm{C}i},...,s_{mi})_i]^2}{n - m}$$

It is a widespread practice to use σ_{fit}^2 to further scale the covariance matrix $\mathbf{c}$

$$\mathbf{c}' = \sigma_{\mathrm{fit}}^2 \mathbf{c}$$

and to then equate the diagonal elements $\mathbf{c}'_{jj}$ to the variances σ_j^2 of the fitted parameters. To derive uncertainties that reflect the desired confidence limits for the fitted parameters, these σ_j^2 are then usually multiplied by the appropriate t from the Student-t statistic. This approach is entirely justified when the initial uncertainties Z_i are unknown (hence implicitly set to 1), in which case σ_{fit} becomes a convenient metric allowing the approximate estimation of σ_j. If, however, the procedure of scaling the covariance matrix $\mathbf{c}$ by σ_{fit}^2 is used in conjunction with a set of known Z_i, the immediate implication is that the relationship of Z_i to σ_i is unknown, not trusted, or ignored, i.e., that Z_i have a meaning only as relative weights for the initial determinations Y_i. If, however, the multiplicative factor t that relates Z_i to σ_i is assumed to be known, then the proper approach is to utilize the unmodified covariance matrix $\mathbf{c}$ (i.e., without additional scaling with σ_{fit}^2), and interpret its diagonal elements as $t^2\sigma_j^2$.

The discussion of the mathematical background that is given above, is, inter alia, based on the assumptions that the initial uncertainty Z_i fairly represents the inherent uncertainty of the determination Y_i, and that the probability of obtaining the value Y_i as the outcome of a determination is fairly described by a normal distribution. If this were indeed the case, then one could simply proceed in one iteration from the initial TN straight to the final set of solutions ΔH_{A}, ΔH_{B}, ΔH_{C}, ..., ΔH_m. The critical evaluation occurring during the initial selection of data, if done properly, will ensure that at least the bulk of the initial data conforms to these assumptions. In practice, and despite all of the care exercised during the initial accumulation of data, some determinations present in the TN will nevertheless correspond to an improbable value, lying far in the tail of the normal distribution. This may occur, for example, if the underlying distribution is significantly different than normal or perhaps because the associated uncertainty is "optimistic" and implies an inappropriately narrow distribution. Such determinations present outliers, which would tend to skew the final results if one were to proceed directly to obtaining the final solutions. The situation can be rectified by preconditioning the TN. Preconditioning is a procedure that utilizes the redundancy existing in the TN to detect and correct the occurrences of outliers in the TN and aims to produce a self-consistent TN. The approach currently adopted in ATcT is the iterative "worst offender" procedure, outlined in the main body of this paper in more detail.

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