Third Millennium Ideal Gas and Condensed Phase Thermochemical Database for Combustion with Updates from Active Thermochemical Tables

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Active Thermochemical Tables

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and
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The thermochemical database of species involved in combustion processes is and has been available for free use for over 25 years. It was first published in print in 1984, approximately 8 years after it was first assembled, and contained 215 species at the time. This is the 7th printed edition and most likely will be the last one in print in the present format, which involves substantial manual labor. The database currently contains more than 1300 species, specifically organic molecules and radicals, but also inorganic species connected to combustion and air pollution. Since 1991 this database is freely available on the internet, at the Technion-IIT ftp server, and it is continuously expanded and corrected. The database is mirrored daily at an official mirror site, and at random at about a dozen unofficial mirror and "finger" sites.

The present edition contains numerous corrections and many recalculations of data of provisory type by the G3//B3LYP method, a high-accuracy composite *ab initio* calculation. About 300 species are newly calculated and are not yet published elsewhere.

In anticipation of the full coupling, which is under development, the database started incorporating the available (as yet unpublished) values from Active Thermochemical Tables.

The electronic version now also contains an XML file of the main database to allow transfer to other formats and ease finding specific information of interest.

The database is used by scientists, educators, engineers and students at all levels, dealing primarily with combustion and air pollution, jet engines, rocket propulsion, fireworks, but also by researchers involved in upper atmosphere kinetics, astrophysics, abrasion metallurgy, etc.

This introductory article contains explanations of the database and the means to use it, its sources, ways of calculation, and assessments of the accuracy of data.

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Acknowledgements

IN MEMORIAM

This publication and database is dedicated to the memories of:

- Prof. William C. Gardiner (1933-2000), professor of chemistry at the University of Texas at Austin; initiator and first publisher of this database

- Sanford Gordon (1920-2001) of NASA Lewis in Cleveland, who investigated and designed the NASA polynomials

- Bonnie J. McBride (1934-2005) of NASA Lewis who wrote the CEA and PAC programs and Compiled and maintained the NASA thermochemical database for 45 years

May they rest in peace.

This database is available in electronic form at:
ftp://ftp.technion.ac.il/pub/supported/aetdd/thermodynamics
and at the mirror site at
http://garfield.chem.elte.hu/Burcat/burcat.html

Introduction

Thermochemistry started, as generally mentioned by different thermodynamicists, with the articles of Mallard and Le-Chatellier (1883) in which the first sentence is the statement: "All combustion is accompanied by the release of heat that increases the temperature of the burned bodies." In 1897 Marcelin Berthelot published his two volume monograph entitled *Thermochimie* in which he summed up 40 years of calorimetric experimentation.

The first textbook to clearly explain the thermochemical properties was Lewis and Randall (1923).

Thermochemical data, actually heats of formation, were gathered, evaluated and published for the first time in the *International Critical Tables* printed in seven volumes between 1926 and 1930 (and the additional Index in 1933). The editor was E.W. Washburn.

In 1932 appears the *ACS Monograph 60* by Parks and Huffman entitled *The Free Energy of some Organic Compounds.*

In 1936 F.R. Bichowsky and F.D. Rossini published *The Thermochemistry of the Chemical Substances*, in which the authors attempted to standardize the available data and publish them at a common temperature of 18 ℃ (291 K) and pressure of one atmosphere.

In 1940, Mayer and Mayer published their monograph *Mechanical Statistics*, in which the method of calculating thermochemical properties from spectroscopic data is explained in detail.

In 1947 Rossini published *Selected Values of Properties of Hydrocarbons*, *NBS Circular 461*, (American Petroleum Institute Research Project 44). This was followed by the famous *NBS Circular 500* (1952), which concentrates on the thermochemistry of organic species, and gives not only enthalpies of formation but also heat capacities (Cp), enthalpies (H_T-H_0), entropies (S) and equilibrium constants (K_c) as a function of temperature.

During the 1950's, the loose leaf compendium of the Thermodynamic Research Center (TRC) at A&M University in Texas appeared as a continuation of API Project 44. In this compendium, thermochemistry as a function of temperature is only a small part of their data that include melting and boiling points, vapor pressures, IR spectra, etc. Although their values are technically reliable, a very serious drawback is the lack of documentation on the data and the calculation methods.

In 1960, the first loose leaf edition of the *JANAF Tables* appeared, but was restricted solely to U.S. government agencies. This first edition is devoted to chemical species involving all the elements, but it contains only a very limited number of organic species. This publication, which became very famous when published as the second (bound) edition (1972), set the standard temperature reference at 298.15 K and published the enthalpy increments (a.k.a integrated heat capacities) as (H_T-H_{298}) instead of (H_T-H_0). This edition of the *JANAF Tables*, with Stull as the main editor, for the first time described in detail their methods of calculating thermochemical properties, which were based mainly on the monograph of Mayer and Mayer [1940]. They also set the temperature range of the tables up to 6000 K in order to assist the needs and request of the space research and industry.

Also in 1960, Thiokol Chemical Corporation published the report

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Thermodynamic Data for Combustion Products by J.S. Gordon, meant for high performance solid rocket propellants.

In 1961 Duff and Bauer published a Los Alamos report, later (1962) summarized in the Journal of Chemical Physics, in which for the first time thermochemical properties of organic molecules, i.e., enthalpy and free energy, were published as polynomials.

In 1963 S. Gordon and B. McBride published the *Thermodynamic Properties of Chemical Substances to 6000 K, NASA Report SP-3001*. This publication revealed for the first time to the public world (because the *JANAF Tables* still had a restricted distribution) the methods of calculating thermo-chemical data for monoatomic, diatomic and polyatomic species, and introduced a thermodynamic value used by engineers but unknown before to chemists: the "absolute enthalpy", which sets the value of $H_T = \Delta_f H_{298} + (H_T - H_{298})$. This publication lists, also for the first time, the thermochemical properties not only in table format but also as 7 coefficient NASA polynomials. The NASA program to calculate thermochemical properties and 7 term polynomials was published by B. McBride and S. Gordon in 1967.

In 1965, NBS started publishing the *Technical Note 270* in a series of booklets where they present heats of formation at 0 K, at 273.16 K and 298.16 K.

In 1969 appeared the book of Stull, Westrum and Sinke, *Thermo-dynamics of Organic Compounds*, where the thermochemical properties of 741 stable organic molecules were published in the temperature range of 298 K to 1000 K.

In 1962 appeared the first edition of the Glushko-Gurvich *Thermodynamic Properties of Individual Substances* (TSIV) in Moscow. This monumental compendium became world known as "Gurvich's Thermochemical Tables" from the further publications in 1978, 1979, 1982, and specifically from the fourth English-translated edition of 1989, which was also followed by further English editions in 1991, 1996, and 1997.

Other thermochemical properties - were published by Barin and Knacke in 1973 and Barin in 1989.

Evaluations of heats of formation for organic molecules and radicals were published by Cox and Wagman (1970), Pedley and Rylance (1977), Domalski and Hearing (1988) and Pedley, Nylor and Kirby (1989) .

Polynomials

Polynomials are mentioned for the fist time by Lewis and Randal as a means to present thermochemical properties such as heat capacity (C_p), enthalpy, and so on, as a function of temperature. The publication of elaborate tables of properties was very problematic in a world where computers were not even imagined. Polynomials seemed a compact way to publish a lot of numbers and also a good way to smooth out measurement scatter of the data. Despite the advantages, polynomials were not used abundantly before the proliferation of computers starting about 1965.

Government agencies such as NASA and various National Laboratories had computers by the end of the fifties, and therefore started using polynomials in order to get thermochemical properties as a function of temperature. The functions were needed in order to calculate equilibrium compositions of reactions, which were extensively used before kinetic programs were available. That was the reason for the publication of Bauer and Duff's paper which included

extensive equilibrium calculations. These authors found out that the full temperature range of 298.15 K to 6000 K cannot be represented by a single polynomial, so they were the first to publish two branch polynomials. There were two sets (each with two branches): one set for heat capacity (C_p) and a second set for the free energy function (*F*). The two branches of the set were not coinciding at any temperature and their use in the 1000 K region included a non-continuity jump.

The thermodynamic group at the NASA Lewis Center in Cleveland, led by Sanford Gordon, undertook a long study in order to investigate the problem of chemical equilibrium [Huff, Gordon and Morrell, 1951; Zeleznik and Gordon, 1960; 1961; 1962]. As a result, a close scrutiny of the polynomialization of the thermodynamic data was also undertaken, and they proposed a solution with two important features: a single set of coefficients could be used for as many properties as possible for a single compound, and the same polynomial form should fit all thermodynamic data for gases, liquids, and solids for all possible chemical compounds. Frank Zeleznik and Sanford Gordon (1961) invented the method of simultaneous regression of the thermochemical properties so that more than one property can be approximated by a single polynomial. These works ended up with the famous NASA 7 term polynomials first published by Zeleznik and Gordon (1962) and McBride *et al*. (1963)

In their first form, the polynomials were fit for two temperature ranges. The first polynomial was fit for the temperature region important for combustion, i.e., 1000-6000 K. The second polynomial was fit for the low temperature region, i.e., 300-1000 K. The

two polynomials were "pinned" at 1000 K. They were constrained to reproduce exactly the 1000 K value, thus assuring that both branches will match at 1000 K without discontinuity. The consequence of this method was that the values at the standard reference temperature of 298.15 K, which were not used to create any constraints, were always reproduced with some small error, depending on the polynomial fit. Later, in 1982, following user's requests, the fitting of the polynomials was slightly changed: the lower branch was extended to 200 K, and the pinning of the polynomials was transferred to the 298.15 K values, while the two branches were still constrained to have the same value at 1000 K.

Because of the need of NASA to calculate properties beyond the 6000 K limit for shuttle orbital reentry problems, the research into the polynomials was extended, and in 1987 a new set of NASA 9 term polynomials were adopted. The foremost quality of these polynomials is that new branches can be added above and below the original range; in addition, their error of reproducing the fitted data was improved between 1 and 2 orders of magnitude. The maximum error at peak temperature of the 7 term polynomials is typically in the range of a tenth of one percent to one percent, while the typical fitting error of the new 9 term polynomials is in the range of one thousandth of a percent and one hundredth of a percent.

The program to calculate thermo-chemical properties (called PAC for Properties and Coefficients) and the corresponding 7 term polynomials were published by McBride and Gordon in 1967, and a new version that calculates the 9 term polynomials was published in 1992.

Other types of polynomials were

also proposed. For example, the Wilhoit (1975) polynomials were intended to allow the extrapolation of the TRC thermochemical properties beyond the 1000 or 1500 K temperature range. These polynomials are used internally for extrapolation by the PAC program as well as the THERM program (see below). The NIST WebBook site prefers the Shomate polynomials. The Gurvich polynomial for the partition function is seldom used in the west. Various series of negative powers of the temperature were also proposed in the past, and very recently [Lanzafame and Messina 2001-2] a series of logarithmic powers of the temperature was proposed. However, none of them got the wide acceptance and extensive use of the 7 term NASA polynomials, mainly due to the existence of big free databases of polynomials such as the one presented here.

The thermochemical properties can be calculated in general with confidence in the fourth and fifth digit in the range of 150-3000 K. But since many engineering problems require the knowledge of data above and below this range, they are provided in the form of 7 term polynomials to 6000 K and as 9 term polynomials from 50 to 6000 K.

The 7-coefficient NASA polynomials can be used to calculate the following functions:

$$\frac{C_p^\circ}{R} = a_1 + a_2 T + a_3 T^2 + a_4 T^3 + a_5 T^4 \quad (1)$$

$$\frac{H_T^\circ}{RT} = a_1 + \frac{a_2 T}{2} + \frac{a_3 T^2}{3} + \frac{a_4 T^3}{4} + \frac{a_5 T^4}{5} + \frac{a_6}{T} \quad (2)$$

$$\frac{S_T^\circ}{R} = a_1 \ln T + a_2 T + \frac{a_3 T^2}{2} + \frac{a_4 T^3}{3} + \frac{a_5 T^4}{4} + a_7 \quad (3)$$

$$\frac{G_T^\circ}{RT} = \frac{H_T^\circ}{RT} - \frac{S_T^\circ}{R} = a_1(1 - \ln T) - \frac{a_2 T}{2} - \frac{a_3 T^2}{6} - \frac{a_4 T^3}{12} - \frac{a_5 T^4}{20} + \frac{a_6}{T} - a_7 \quad (4)$$

It should be noted that the value H_T° obtained from the polynomials is the "engineering enthalpy" defined as

$$H_T^\circ = \Delta_f H_{298}^\circ + \int_{298}^{T} C_p^\circ \, dT \quad (5)$$

Similarly, the G°/RT functions of the molecules in a reaction can be used directly to compute the reaction's equilibrium constant in terms of concentrations through

$$K_c = (RT)^{-\Delta v} \exp \left(\begin{array}{c} \Delta a_1 (\ln T - 1) + \\ \dfrac{\Delta a_2 T}{2} + \dfrac{\Delta a_3 T^2}{6} + \\ \dfrac{\Delta a_4 T^3}{12} + \dfrac{\Delta a_5 T^4}{20} - \\ \dfrac{\Delta a_6}{T} + \Delta a_7 \end{array} \right) \quad (6)$$

where the change in mole number is $\Delta v = \Sigma v_j$ and the coefficient changes are $\Delta a_I = \Sigma v_j a_{ij}$. The summations are over all the reactant and product species j with the stoichiometric coefficients v_j being positive for products and negative for reactants.

The 7 term polynomials actually include 15 constants. The first set of 7 constants belongs to the 1000-6000 K polynomial, the second set of 7 constants belongs to the 200-1000 K polynomial, and the fifteenth constant is $H_{298}/R \equiv \Delta_f H_{298}/R$. The latter value (and the corresponding position within the polynomial format) is not used by most other programs, such as CHEMKIN, and therefore does not interfere with their calculations.

The 9-constants polynomials can be used to calculate the following functions:

$$\frac{C^{\circ}_p}{R} = a_1 T^{-2} + a_2 T^{-1} + a_3 + a_4 T +$$

$$a_5 T^2 + a_6 T^3 + a_7 T^4 \tag{7}$$

$$\frac{H^{\circ}_T}{RT} = -a_1 T^{-2} + \frac{a_2 \ln T}{T} + a_3 + \frac{a_4 T}{2} +$$

$$\frac{a_5 T^2}{3} + \frac{a_6 T^3}{4} + \frac{a_7 T^4}{5} + \frac{a_8}{T} \tag{8}$$

$$\frac{S^{\circ}_T}{R} = -\frac{a_1 T^{-2}}{2} - a_2 T^{-1} + a_3 \ln T + a_4 T +$$

$$\frac{a_5 T^2}{2} + \frac{a_6 T^3}{3} + \frac{a_7 T^4}{4} + a_9 \tag{9}$$

$$\frac{G^{\circ}_T}{RT} = \frac{H^{\circ}_T}{RT} - \frac{S^{\circ}_T}{R} = -\frac{a_1 T^{-2}}{2} +$$

$$\frac{2a_2(1 - \ln T)}{T} + a_3(1 - \ln T) - \tag{10}$$

$$\frac{a_4 T}{2} - \frac{a_5 T^2}{6} - \frac{a_6 T^3}{12} - \frac{a_7 T^4}{20} + \frac{a_8}{T} - a_9$$

and also K_c, following a similar philosophy as given above for the 7 term polynomial.

Thermodynamic Calculations

All calculations of thermodynamic quantities related to the partition function (such as heat capacity, entropy, enthalpy increment, etc.) and polynomialization in this database were performed using the McBride and Gordon PAC program. (Gordon and McBride 1967, 1992). For gas-phase species with molecular information the rigid-rotor-harmonic-oscillator (RRHO) method was used, and, if anharmonic information was available, non-rigid-rotor-anharmonic-oscillator (NRRAO) was used. In a very few cases both RRHO and NRRAO are given. For species where the direct tables from another source were used the READIN method was utilized.

Over the years, the PAC program has been changed and extended and new documentation published (McBride and Gordon 1992). At least 4 versions of this program were used to produce the polynomials listed. Those prepared before 1984 were produced with the PAC3 version in which internal rotations were not calculated simultaneously and the corresponding contributions had to be added separately. PAC4, released in 1984, included the possibility to compute the contributions of internal rotations automatically.

If a set of data is fitted by two polynomials valid over different temperature ranges, the polynomials could in principle meet at different temperatures for different species (Burcat 1984). Ritter's program (Ritter 1990) optimizes this temperature and pins the two polynomials at the given value. However, most programs that use the thermodynamic polynomials prefer a constant pinning value. In the PAC programs, the temperature at which the polynomial branches switch was arbitrarily set to 1000 K. Before PAC4 the polynomials were pinned to the tabular value of 1000 K and therefore reproduced it exactly. In that case, the values at 298 K obtained from the polynomial are not the original tabular values, but slightly different (depending on the local error of the polynomial coefficients). This fact is mentioned in the directory table (Table 6) with an asterisk (*). In the latest versions, PAC90 PAC97 and PAC99 the lower range polynomial is pinned at 298.15 K to the tabular values and at 1000 K the two polynomials are pinned to each other (thus having the same "hanging" value, which is not necessarily the tabular value). These versions also include Wilhoit type extrapolations, as discussed by Burcat (1984), and optional use of estimated additivity group properties as described by Stein (1985).

Sources of Data

A large number of sources were used for the present compilation. Where more than one source was available for a species, the value that appeared to be the most reliable (at least at the date of calculation of the polynomial coefficients) was selected. If no thermodynamic data were available in known tabulations or in the archival literature, the literature was searched for experimentally or quantum mechanically calculated vibrational frequencies and moments of inertia. If such data were not available, then approximation methods were used in order to estimate the molecular constants.

Some estimations were made using the parent molecule method, in which vibrational frequencies of radicals were estimated from the vibrations of the parent molecule by deleting relevant vibrations.

Other methods of estimation included the Benson (1976) group additivity method, as used by Stein (1985) in both PAC97 and the NIST 1991 *Structure and Database Estimation Program* (Stein *et al*., 1991; Stein 1994) and Ritter and Bozzelli's (1990) method in the *Therm* program (Ritter 1990) which also uses additivity groups but in a slightly different manner. In France, a third program exists, *Thergas*, by Muller *et al*., (1995). This program uses Benson's additivity method and is based on the *CHETAH* program (Frurip *et al*., 1989).

The difference between the Ritter and Bozzelli method and Stein's method is that the first uses discrete point values for each "group" value, adds the separate values for each temperature and then fits a polynomial for the final results using one of three possible extrapolation methods, Wilhoit's method among them. Stein's (1985) method is not fully described. It apparently produces a polynomial for each of the additivity group fragments, and adds the different polynomials for the estimated final species.

In the last decade semi empirical programs such as the *MOPAC* [Stewart 1989, 1990, 1993] package became widely available, followed by more accurate *ab initio* DFT and wavefunction methods that can be performed with *Gaussian*, *MOLPRO, GAMESS* and other electronic structure computation program packages.

Among the methods that calculate the species electronic structure, the density functional theory (DFT) methods have gained an important position, specifically the Becke (1993) exchange functionals coupled with the Lee-Yang-Parr (1988) function widely known as B3LYP. The composite *ab initio* G3 theory (Curtiss *et al*., 1998) and it's variant G3B3 (Baboul *et al*., 1999) are able to achieve very high accuracy (with a 95% confidence limit that is generally around ± 2 kcal/mol or better), without requiring (at least for small and medium-sized species) an exorbitant computational effort. These methods are geared up to calculate the enthalpy of formation of the species through the atomization energy, producing also the other needed molecular properties such as geometry and vibrations.

The *ab initio* G3B3 method optimizes the geometry and calculates the molecular frequencies using the DFT B3LYP method. These compare very well with experimental IR and Raman measurements. The enthalpies of formation are then calculated using a composite approach that performs a sequence of calculations at various levels and with various basis sets, effectively estimating the energies at the QCISD(T) level using a large basis set (G3Large).

Thus, the method can calculate the spectroscopic and thermodynamic properties of radicals, which are otherwise very hard to measure experimentally. Using commodity computers (such as PCs), the practical limitation is of the order of 10 "heavy" atoms (i.e., all elements other than hydrogen) due to limitations in memory and computation time. Other *ab initio* methods such as W2 are even more restricted.

In the present database, a substantial effort was undertaken to replace as many as possible of the old version estimates based on additivity methods with new and significantly more accurate G3B3 values. However, many of the species in the database exceed the 10 heavy atom limit. For these bigger species, semi empirical methods (usually PM3 and sometimes AM1) were used to calculate vibrations and moments of inertia, and the enthalpies of formation had to be estimated by the additivity approach, as in earlier versions.

The present edition also started incorporating some of the values that are now available from Active Thermo-chemical Tables (*vide infra*).

Ab initio and other Calculations
The G3//B3LYP (a.k.a. G3B3) calcula-tions were performed using *Gaussian 03* package. The input to this program is prepared using Chem3D to initially construct and equilibrate the species, using sequentially the minimum energy conformation as obtained via Molecular Mechanics and MOPAC 2000 packages.

The G3B3 calculations were performed by explicit sequencing following the procedure of Baboul *et al.* (1999). Thus, the geometry of the species was optimized and its frequencies were calculated at B3LYP/6-31G(*d*) level. The optimized geometry was subsequently used to perform single point computations at the QCISD(T)/6-31G(*d*), MP4/6-31+G(*d*), MP4/6-31G(*2df,p*), and MP2(full)/G3Large levels (with externally specified basis set in the latter step). The Gaussian output was harvested using a script that extracted the needed values, performed the prescribed arithmetic on the various components of the electronic energy, applied the appropriate higher-level corrections for molecular species and (separately) higher-level corrections and spin-orbit corrections for atoms, computed the zero-point energies from B3LYP frequencies scaled by 0.96, etc. The end-product of the script was a compact listing giving all the relevant components of the electronic energy and spectroscopic constants, as well as atomization energies at 0 K and enthalpies of formation at 0 K and 298.15 K. The atomization energy and enthalpies of formation was computed using standard enthalpies of formation of atoms and enthalpy increments for the elements in reference states (Cox *et al.*, JANAF, Gurvich *et al.*). The procedure was extensively tested beforehand by using it to reproduce a large sample of the values given by Baboul *et al.* (1999).

The Internal Rotation Problem
Ideal gas values for the heat capacity, enthalpy increment, and entropy can be computed from the partition function if sufficient spectroscopic data (rotational constants, frequencies, and low-lying excited electronic states) are available. The rotational constants (i.e. geometry) and frequencies can be obtained with reasonable accuracy from various *ab initio* computations. However, unless the barrier happens to be available from experimental measurements, the contribution of hindered rotors is the one

that is the most difficult to obtain, unless one carries out additional computations along the internal rotor coordinate. Please note that the hindered rotor barrier is not explicitly obtained from G3B3 (and similar) type of computations of the lowest energy conformer. In order to, for example, convert the 0 K enthalpy of formation to the 298 K value, such methods use implicitly the pseudo-vibration approach for the internal rotor.

Aside from the pseudo-vibration approach, the most popular method for calculation of the rotation energy levels and wavefunctions of the internal rotation is by representing the hindered rotor potential via the expansion introduced by Lanne [Lewis *et al.*1972], who used the six-term summation:

$$V = \frac{1}{2}\sum_{n=1}^{6} V_n (1 - \cos n\phi) \qquad (11)$$

Often the six terms can however be approximated by one term only (e.g., V_3 for a methyl rotor) even when the symmetry of the species would require more terms. The value of the single term is typically estimated by comparison to similar species for which such term is either known or already estimated by prior considerations. This shortcut is followed by many thermodynamicists due to the relatively small contribution of the internal rotation to the whole entropy value. This is however a potential point of error (having a tendency to affect the computed entropy somewhat more visibly than the corresponding enthalpy increment or heat capacity), and the user is warned about this simplification.

Standard Enthalpies of Formation

Standard enthalpies ("heats") of formation of all species can be divided into three categories:
a) those that were experimentally measured either by combustion calori-

metry or by determining the enthalpy of a reaction involving the target (and other) species;
b) those estimated on the basis of experimental values of other (similar or related) compounds;
c) those estimated on the basis of other estimated compounds or structural groups. Standard enthalpies of formation are quoted and re-quoted by different authors, making it sometimes challenging to find out to which of the three categories the quoted $\Delta_f H°_{298}$ value belongs. When the measured values of individual compounds change with time due to better experimental systems or to errors found in previous measurements, it causes a need to change the $\Delta_f H°_{298}$ values whose determination or estimation was based on those values. However, there were no convenient means to perform these corrections other than tedious and continuous manual examination of each individual $\Delta_f H°_{298}$ value. The differences in the auxiliary values used to extract the enthalpy of formation of the species from the measured quantity are frequently at the core of disputes between groups of researchers claiming a different heat of formation for an important species. In this compilation, many decisions as to which value to adopt had to be done in the past arbitrarily for lack of established criteria.

These types of problems, together with other disadvantages connected to the traditional sequential approach to evolving enthalpies of formation, are being currently successfully addressed by the *Active Thermochemical Tables (ATcT)* approach [Ruscic, 2004, and Ruscic *et al.*, 2004], into which this database is now being integrated.

Active Thermochemical Tables

Active Thermochemical Tables (ATcT) are a new paradigm that catapults

thermochemistry into the 21st century. As opposed to traditional sequential thermochemistry, ATcT provides reliable, accurate, and internally consistent thermochemistry by utilizing the Thermochemical Network (TN) approach.

The traditional approach is geared up to determine the enthalpies of formation of the target species using a sequential procedure. In this procedure, one and only one species is examined during each step. The available measurements (and/or computations) that link the target species to those (and only to those) determined in previous steps are examined. From these, the "best" determination (or, occasionally, the average of a few determinations that appear to be of similar quality) is selected and used to obtain the enthalpy of formation of the target species at one temperature. The spectroscopic data is then used to compute the temperature dependence of the enthalpy and the remaining complement of thermochemical functions pertinent to the target species. At that point the thermochemical properties of the target species are "frozen" and the procedure moves on to the next step, focusing on a new target species.

The primary disadvantage is that the resulting tabulation of enthalpies of formation stores for any species only the final value for the enthalpy, which is in reality connected to other enthalpies across the table via a maze of hidden progenitor-progeny relationships, making it next to impossible to update the resulting data with new information. Namely, even if, for example, a newly-measured bond dissociation energy is used to revise the enthalpy of formation of some species, there are generally other species in the table that are pegged to the old value and would also need to be revised. Which those are is not clear without investing a very laborious manual effort that examines each and every species in the tabulation.

In addition, the uncertainties obtained in the traditional approach typically do not properly reflect the complete knowledge that was available at the time the tabulation was created. For example, some of the existing knowledge is simply ignored (or taken only as a secondary check) because it did not make it into the subset of "best" determinations. Since there is no feedback to values obtained in the previous steps, the relevant dependencies that are used in later steps in the procedure (and involve directly or indirectly the species that were determined in previous steps) do not contribute to the quantification of the uncertainties in earlier steps nor do they help improve the reliability of values that are already frozen. In short, available knowledge is used only partially.

As opposed to the sequential approach, ATcT are using the Thermochemical Network (TN) approach. The TN does not store enthalpies of formation of various species as such; rather, it stores the various relationships between the enthalpies as given by the actual measurements and/or computations, creating a network of thermochemical interdependencies. In order to obtain the desired enthalpies of formation, the TN is solved simultaneously for all the species it describes, producing a complete set of thermochemical values that are entirely mutually consistent. Furthermore, the dependencies stored in the TN are not based on the selected "best" subset of determinations. Rather, *all* available determinations from the literature are stored in the network. Since those are not necessarily self-consistent (because some of the quoted uncertainties are "optimis-

tic", i.e., some determinations are not as correct as the uncertainty might imply, or, are, even in fact "wrong"), the TN solution is preceded by a statistical analysis and evaluation of the determinations that span and define the TN. The statistical evaluation of the determinations in the TN is made possible by redundancies in the TN, such as competing measurements of the same enthalpy of reaction, and/or alternate network pathways that interrelate the participating 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 the best possible use of all knowledge present in the TN. This results in significantly better values that the traditional sequential approach, since it uses efficiently *all* the available knowledge and also relies on a statistical analysis. The significantly increased reliability and accuracy of the values obtained from the TN approach manifests itself through uncertainties (which are given as 95% confidence limits, as customary in thermochemistry) that are typically several times smaller than the equivalent sequential values that could be obtained by the traditional sequential approach.

On top of the dramatically improved reliability, accuracy, and consistency of the resulting thermo-chemical values, ATcT offer a number of features that are neither present nor possible in the traditional sequential approach. With ATcT, new knowledge can be painlessly propagated through all affected thermochemical values. Namely, a new measurement can be simply added to the TN, followed by the automatic analysis and solution of the TN, producing a new (revised) complement of thermochemical values for all the species present in the network, thus fully propagating the consequences of the new measurement through all the affected values.

ATcT also allow 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 knowledge base of ATcT is organized in a series of "Libraries". The Main Library contains the Core (Argonne) Thermochemical Network that is currently being developed. At the moment (ver. 1.048), this TN contains fully networked data on > 600 species through > 3500 relevant determinations and is growing on a daily basis. Most of the initial species included in this TN are relatively small and play the role of "hubs" in the network (significantly overlapping with the notion of "key" CODATA species), but as the network grows, larger species are being introduced. Besides the TN, the Main Library also contains the relevant spectroscopic data for gas-phase species and tabular data for condensed-phase species that is needed to compute the heat capacity, enthalpy, increment, entropy, the temperature dependence of the enthalpy/Gibbs energy of formation, etc. As new data is introduced in the TN in the Main Library, a new set of solutions of the TN is periodically computed, producing a new version and storing the prior version into the archives (following an elaborate archival system).

Auxiliary libraries (e.g. CODATA Library, Gurvich Library, JANAF Library, etc.) are more static in nature and contain non-networked data needed to reproduce the values in various historical tabulations for ready-reference purposes.

We are currently undertaking the effort of assimilating the present database as one of the auxiliary ATcT Libraries. Though not containing networked data *per se*, the special feature of this Library will be the ability of getting an automatic update whenever new and/or better information is available through ATcT. Specifically, each time a new solution is obtained from the networked data in the Main Library, the relevant species in this database will be also updated.

At the current stage of its development, the Core (Argonne) Thermochemical Network of ATcT is still concentrating on defining as accurately as possible various "key" (typically small) species and their ions. Consequently, the overlap with the present database is modest. This will, however, gradually change as the ATcT TN grows.

In anticipation of the full merger with automatic update capabilities, some of the values in this database have been manually replaced by the new ATcT values using the ATcT kernel ver. 1.25 and the Core (Argonne) Thermochemical Network ver. 1.048. Whenever the difference between the ATcT and the prior value of the enthalpy of formation was larger than ~1 kJ/mol (or if it was a new species that was not contained in the previous edition of this database), a new polynomial was calculated. In view of the laborious effort involved in manually updating the polynomials, and in anticipation of the development of fully automatic updates, when the difference was smaller than ~1 kJ/mol, the ATcT value was simply added to the comments preceding the polynomial, but the existing polynomial was kept unchanged.

Accuracy of Enthalpies of Formation
Though barely at its beginning, ATcT has already produced for a number of "key" species significantly more accurate thermochemical values, thus considerably increasing the number of species known to very high accuracy. Nevertheless, in general, only a small minority of species of interest in combustion can be assigned standard enthalpies of formation with uncertainty limits so narrow that for combustion modeling purposes they may be taken to be exact (Cox *et al*., 1989; Cox and Pilcher 1970; Cohen 1996). The most accurately known of all (aside from, of course, the elements in their reference states, for which the value 0 is defined to be exact) are those based on carefully recorded molecular electronic spectra supplemented by quantum-mechanical analysis. Among those the hydrogen atom stands out, and a few diatomic and triatomic species whose electronic spectra have been successfully analyzed to accurately establish the dissociation limit also belong in the exact category. An overview of the uncertainties of the standard enthalpies of formation of the key combustion-relevant atomic to

Table 1. Standard enthalpies of formation in kJ/mol at 298.15 K for small gas-phase species of interest in combustion. (All species from Active Thermochemical Tables v 1.25 using C(A)TN v. 1.048, except the sulfur species which are from the NASA database.)

Species	$\Delta_f H_{298}$
C(g)	717.065 ± 0.146
H(g)	217.997 ± 0.0001
O(g)	249.229 ± 0.002
N(g)	472.459 ± 0.044
S(g)	277.17 ± 0.25
Cl(g)	121.302 ± 0.001
NO(g)	91.097 ± 0.084
CO(g)	-110.538 ± 0.026
H_2O(g)	-241.815 ± 0.031
CO_2(g)	-393.472 ± 0.014
SO_2(g)	-296.84 ± 0.21
NO_2(g)	34.025 ± 0.085

triatomic species that have been exhaustively studied by calorimetric and spectroscopic methods is given in Table 1. One sees that the accuracy benchmark set by this group of species (in effect setting a standard of what can be achieved in measuring or computing standard enthalpies of reaction) is in the vicinity of 0.1 to 0.2 kJ/mol.

It should be noted that the new ATcT values are expected to bring about significant overall improvements in the accuracy and reliability of the available thermochemistry. However, keeping in mind the present extent of the Core (Argonne) Thermochemical Network that is currently under development, the majority of species currently covered in this database are not (as yet) available through the TN approach, and their values come from traditional sources. Here we would like to make a few cautionary comments on the state of affairs with respect to traditional sources.

Overall, the number of species important in combustion for which experimental values of standard enthalpies of formation can be assigned is comparably small. All are based on chemical reactions to which enthalpy changes of reaction can be assigned with high accuracy either calorimetrically or from the temperature dependence of equilibrium constants. As far as stable molecules of the elements carbon, hydrogen, oxygen and nitrogen are concerned, it is fortunate that combustion reactions themselves serve for this purpose, as the standard enthalpies of formation of the combustion products. Carbon dioxide and water have been painstakingly evaluated and reactions can usually be arranged to occur with accurately measured stoichiometry (Cox and Pilcher, 1970).

Even in the most favorable cases, however, the error bounds that have to be accepted are larger than one would wish. This is illustrated in Table 2, adapted from Cohen and Benson (1992), who give references to the archival literature. Here one sees that the "best available" standard enthalpy of formation values for the small hydrocarbons come with error ranges that imply significant uncertainty in equilibrium constants. (A $\pm$ 1 kJ/mol uncertainty in the enthalpy or Gibbs energy change of a reaction at 1000 K implies an uncertainty of $\pm$ 12 % in its equilibrium constant.)

Table 2. Standard enthalpies of formation in kJ/mol at 298.15 K for small hydrocarbons (After Cohen and Benson, 1992).

Species	Bomb Calorimeter	Flame Calorimeter
CH_4	-74.85 $\pm$ 0.29	-74.48 $\pm$ 0.42
C_2H_6	-84.68 $\pm$ 0.50	-83.85 $\pm$ 0.29
C_3H_8	-103.89 $\pm$ 0.59	-104.68 $\pm$ 0.50
n-C_4H_{10}	-127.03 $\pm$ 0.67	-125.65 $\pm$ 0.67
i-C_4H_{10}	-135.60 $\pm$ 0.54	-134.18 $\pm$ 0.63

Not only are the uncertainty ranges asserted by the evaluators larger than one would wish, the differences between the values obtained with the two most trustworthy calorimetric techniques are seen on close inspection to differ from one another by more than the sum of the stated uncertainty ranges for three of the five cases. Aside from these discrepancies (which can now be successfully treated and resolved via the TN analysis of ATcT), the asserted uncertainty ranges are about twice as large as for the values listed in Table 1. The values are less well known for most of the other stable species of interest in combustion, and still less well known for unstable ones. Among the unstable species, the thermochemistry of free radicals has attracted particular interest in

combustion modeling because of their roles as chain centers.

An overview of current knowledge of the standard enthalpies of formation of some of the common ones is given in Table 3. In contrast to the stable hydrocarbons, where the standard enthalpy of formation is based on one or another of the direct calorimetrical methods, values for radicals come from all sorts of very difficult measurements ranging from photoionization mass spectroscopy to reaction rates. It is no surprise that the results are more contentious and less accurate. In Table 3, the uncertainty ranges can be seen to be typically an order of magnitude greater than for stable hydrocarbon values except where the Active Table can help.

For hydrocarbons and their various derivatives containing oxygen and nitrogen atoms, a long history of thermochemical investigation has left a legacy of experimental standard enthalpy of formation values. (Some 3000 have been compiled by Pedley et al., 1986).

The uncertainty level of this legacy varies considerably because of the fluctuating care given to the (mostly) calorimetric measurements and problems of reagent purity and reaction stoichiometry. From early on there have been successful efforts to systematize the database in terms of molecular structure (Reviewed in detail by Cox and Pilcher, 1970). As a result, one can compute a standard enthalpy of formation value for "ordinary" compounds that have not been studied experimentally with almost the same confidence that one can place in the experimental values themselves. A large number of entries in the present tabulation have been derived by the NIST or THERM group additivity programs that offer current embodiments of this idea. The capabilities and limitations of

Table 3. Standard enthalpies of formation in kJ/mol at 298.15 K for common radicals. Values accepted by the IUPAC Task Force for Thermochemistry of Radicals of Relevance in Combustion and Atmospheric Chemistry, 2005.

Species	$\Delta_f H_{298}$
OH(g)	37.34 ± 0.04
CH(g)	596.30 ± 0.25
CN(g)	438.81 ± 0.52
NH(g)	358.76 ± 0.37
SH(g)	141.87 ± 0.52
CH_2OH(g)	-17.18 ± 0.37
CH_3O(g)	20.257 ± 0.42
HO_2(g)	12.296 ± 0.25
CHO(g)	42.296 ± 0.3
CH_2(g)	391.465 ± 0.27
CH_3(g)	146.582 ± 0.1
C_2O(g)	291.04 ± 63
C_2H(g)	568.06 ± 0.31
C_2H_3(g)	296.61 ± 0.92
C2H5(g)	118.66 ± 2
C_3H_3(g)	339 ± 4
C_3H_5(g)	171 ± 3
n-C_3H_7(g)	101.32 ± 1
i-C_3H_7(g)	90.19 ± 2
C_6H_5(g)	339.7 ± 2.5

group additivity methods for stable organic molecules have been reviewed by Pedley et al., (1986) and Cohen (1996); discussions of the issues involved in making group additivity estimates for radicals are given by Muller et al., (1995) and Lay et al., (1995).

Unfortunately, many of the most interesting molecules and radicals used in combustion modeling are not ordinary at all, but have highly strained rings or electronic structures that are not well represented in the experimental database used for setting group additivity parameters. For such molecules and radicals we recommend to abstain from use of the group additivity methods anyway, and to prefer instead ab initio

calculations or, if that appears infeasible, as in case of big species, semi-empirical or semi-theoretical molecular electronic structure calculations.

Since the enthalpies of formation seem to be the most problematic of all the thermochemical values, Table 6 is dedicated to this quantity, where we stress the errors if available. In Table 4 we mention additional values for some species in curled parenthesis.

Accuracy of Partition-Function Related Thermochemical Values

As in all thermochemical compilations, the species properties were calculated with varying degrees of accuracy. Some of the species, such as the element N_2 or the molecule HD, were calculated using very high accuracy methods, while others were calculated using approximation methods.

The rigid-rotor-harmonic-oscillator (RRHO) approximation method was accepted as the standard for polyatomic species, and widely adopted by JANAF, TSIV, Thermodynamic Research Center, Stull, Westrum and Sinke (1969) compilations, and many others. Where applicable, this method was augmented by supplementary internal rotation or other contributions as used by various authors. These calculations are considered here as "accurate" values.

The extrapolation methods used, either Wilhoit or Ritter and Bozzelli, were found to give generally good results, and their maximum deviation from standard RRHO calculations for $C_p(T)$ is usually below 0.5%. The errors, however, are greater for estimated species. It is assumed that the parent molecule method used for estimation of radical species by the authors (Burcat 1982, Burcat *et al.*, 1979, 1983, 1985) has a maximum error of ±3 % for $C_p(T)$ while Benson's group property method used by Stein and Ritter and Bozzelli gives a maximum error for unknown species which is in the ± 8% range for $\Delta_f H_{300}$. These are maximum values, and for most cases the errors are by far lower (see Reid, Prausnitz and Poling, 1988, p. 196).

The G3B3 method was assigned a standard error value of ± 8 kJ/mol which is twice the value of the mean absolute deviation (MAD) for this method, quoted as slightly less than 1 kcal/mol by Baboul *et al.*, (1999).

It should be emphasized that the accuracy of the fit given by the coefficients tabulated on the Internet varies considerably from one species to the next. For essentially all purposes in combustion modeling, however, the accuracy of the polynomials with these coefficients is much better than the uncertainties of the modeling introduced by other sources.

The accuracy by which the given polynomials represent the original calculated tabular values is given, where pertinent, in the header preceding the polynomial. This accuracy value is given in terms of the maximal error among the three fitted properties, C_p, entropy and absolute enthalpy. C_p has in most cases the maximal error, and the temperature at which this error was found is given. A large fitting error usually indicates that the underlying tabulated values were not smooth.

Because of different machine round-offs, word lengths, and values of constants used, it is only seldom that the exact original values calculated by the authors are reproduced by a different user. Accuracy in the reproduction of the original values from polynomials can be improved if double precision computation is used (on other than 64 bit word machines), and if the polynomial is

calculated in the recursive form such as:

$$CP = (((A5 * T + A4) * T + A3) * T + A2) * T + A1 \qquad (12)$$

Critical Evaluation of the Polynomials

The thermodynamic data represented by the polynomials were critically evaluated according to their quality aside from the value of the standard enthalpy of formation $\Delta_f H^\circ_{298}$ that was assigned to the species, which must be evaluated separately as explained above. Five groups were identified and marked **A** to **F**.

A designates the most accurate calculations and is reserved for the `direct summation' method, for diatomic molecules and non-rigid-rotor-anharmonic-oscillator (NRRAO) approximations for which anharmonicity corrections were included.

B denotes regular RRHO approximation calculations, including internal rotations where pertinent and/or other electronic excitations. The `parent' method for the approximation of radicals is included in this category.

C includes species whose thermodynamic properties were calculated by the RRHO method but some shortcuts were taken. RRHO calculations with estimated vibrational frequencies are included in this category, as are cases where the internal rotor was neglected and a free rotor was used instead. Some of the data originating with TRC/API tables are considered in this category, since the way they were calculated is not clear.

D and **E** categories were reserved for data estimated from group contributions. The normal estimated species were included in the **E** group, while if additional experimental information was used, then the **D** label was assigned.

The **F** category is reserved for very rough approximations using Benson's additivity groups or other types of estimations with very large error limits.

Ion Conventions

Unfortunately, there are two different conventions for expressing the enthalpies of formation of ions. One is the "thermal electron" convention, the other the "stationary electron" convention. In the "thermal electron" convention, the enthalpy increment H_T-H_0 of the "electron gas" is equal to 2.5 RT, while in the "stationary electron" convention the enthalpy increment is zero at all temperatures. This choice affects the enthalpies of formation and the Gibbs energies of formation of all ions, but not the other quantities, such as entropies.

For historical reasons, this database adheres to the "thermal electron" convention, which is also the convention adopted by the JANAF Tables, the NBS Tables, and the Gurvich Tables.

Please note that most ion chemists use the "stationary electron" convention, as does the compilation of ion thermochemistry of Lias *et al.* (and hence also the NIST WebBook, which implicitly uses the values for ions from Lias *et al.*, though they are seldom given explicitly). Please also note that commingling values from the two conventions results in serious errors. Hence, it is essential to have the values for all charged species expressed within the same convention. As long as all values that are combined to compute the thermochemistry of a chemical reaction are within the same convention, the resulting enthalpies of reactions, Gibbs energies of reactions, equilibrium constants, etc. are the same in both conventions, except when the "electron gas" (which is treated differently in the two conventions) is explicitly involved as one of the reactants

or products. (Parenthetically, ATcT can work under either convention, though the default is the "stationary convention" preferred by ion chemists.)

The conversion of enthalpies of formation from one convention to the other is quite trivial. At 0 K, the enthalpies of formation are identical in both conventions. At any other temperature, the value for the enthalpy of formation belonging to the "stationary electron" convention can be converted to the value belonging to the "thermal electron" convention by adding the quantity $q \times 2.5RT$ (= $q \times 6.197$ kJ/mol at 298.15 K), where q is the charge of the ion:

$$\Delta_f H_T^{thermal.conv.}(\text{ABC}^{+q}) =$$
$$\Delta_f H_T^{station.conv.}(\text{ABC}^{+q}) + q\, 2.5\, RT$$

$$(13)$$

$$\Delta_f H_T^{thermal.conv.}(\text{ABC}^{-q}) =$$
$$\Delta_f H_T^{station.conv.}(\text{ABC}^{-q}) - q\, 2.5\, RT$$

For example, $\Delta_f H_{298}(\text{H}^+)$ = 1530.047 kJ/mol under the "stationary electron" convention. Adding 6.197 kJ/mol produces 1536.244 kJ/mol, which is the correct 298.15 K value under the "thermal electron" convention, as used in this database. Similarly, $\Delta_f H_{298}(\text{H}^-)$ = 145.228 kJ/mol under the "stationary electron" convention. Subtracting 6.197 kJ/mol (since the charge is -1) produces 139.031 kJ/mol, which is the correct value under the "thermal electron" convention.

What is New in the Present Edition
The present version of the database has several new features, beside an increased number of species and the replacement of about 200 **E** and **F** species (see above) with more accurate and reliable data. Unpublished data from *Active*

Thermochemical Tables (ATcT) ver. 1.25 using the Core (Argonne) Thermochemical Network ver. 1.048 have been included where available.

An additional separate database was initiated (Table 5) to contain NASA 9 coefficient polynomials, and to serve as an enlargement of the original NASA database of Bonnie McBride (http://cea. grc.nasa.gov). This database contains polynomials with three temperature intervals but unlike the NASA polynomials, these intervals are 50-200 K, 200-1000 K, and 1000-6000 K. Therefore these can serve for low temperature calculations.

In the main database Table 4 (file burcat.thr) the CAS (Chemical Abstracts) species identification number was added to all species where available.

In the index table Table 6 (hf.doc) we have added the value of $\Delta_f H_0$ besides $\Delta_f H_{298}$ and also the value of H_{298}-H_0.

An important addition to the database is a program written by R. Pinzon and E. Burcat in Phyton (2.4 #60), which allows automatic extraction of data from the main file (burcat.thr) including the data in the header of the polynomial species into an XML file. The XML file produced from our database presented in this printed edition is available via the Net.

Species not Included in this Database
About 1300 species were included in this compilation. Finding species not included in the compilation may be a tough task.

A) If you are looking for a simple hydrocarbon, paraffin, olefin, or a cyclic specie, there are good chances to find it if it has less than 20 carbon atoms in either the TRC (Thermodynamics Research Center) compilation or in the old Stull, Westrum and Sinke (1969) book. Additional sources are the articles

appearing periodically in the Journal of Physical and Chemical Reference Data.

B) If you are looking for a more complex specie or a radical, the available sources are the computerized databases of NIST Structures and Properties Database # 25 ver 2.0 1994, and the WebBook (Afeefy *et al.*), or periodic articles in the literature. There exists a database of molecular properties by Carl Melius that includes 3700 species. Many of these species are transition states. The Melius thermochemical tables are not available to the public, and only limited thermochemical information ($\Delta_f H_{300}$ and $\Delta_f G_{300}$) was published with his molecular structure data. The published thermo-chemical values calculated with the 1987 BAC/MP4 method are of low reliability.

C) For a solid or liquid species (not ideal gas) like $CaSO_4$ the place to look for is the JANAF compilation or the Barin (1995) compilation or the report of McBride, Gordon and Reno, NASA TM 4513 (1993).

D) Silicon containing species can be found in the CHEMKIN database (Kee *et al.*, (1992)). Sandia has initiated a database by M. Allendorf that includes presently Al, B, Si and Sn species calculated with the BAC/MP4 method. Other organometalic species of Ga and As can be found in an article by Tirtowidjojo and Pollard (1986).

E) Ion of simple bi- and triatomic species can be found in JANAF. The other compilation that mentions $\Delta_f H_{298}$ for ion species for some of the molecules and radicals included, is the above mentioned NIST S and P #25 computerized database (1994). The information therein was taken from Lias *et al.*, Journal of Physical and Chemical Reference Data, Vol. 17, (1988), Supplement # 1.

Conversion Factors
The following conversion factors were used in the present compilation:
1 cal = 4.184 J
R = 8.314472 J mol^{-1} K^{-1}
R = 1.987207 cal mol^{-1} K^{-1}
1 eV = 23.06055 kcal mol^{-1}
1 eV = 8065.537 cm^{-1}
1 kcal/mol = 349.7547 cm^{-1}
1 cm^{-1} = 2.859146 cal mol^{-1}
1 cm^{-1} = 29.9792458 GHz
1 Hartree = 627.5101 kcal mol^{-1}
1 Hartree = 2625.502 kJ mol^{-1}
1 Bohr = 0.5291772 Å
1×10^{-39} g cm^2 = 21.50545 amu Bohr^2
1×10^{-39} g cm^2 = 6.022137 amu Å^2
B/cm^{-1} = 60.19969/[I_B/(amu Bohr^2)]
B/cm^{-1} = 16.85763/[I_B/(amu Å^2)]
B/cm^{-1} = 2.799277/[I_B/(10^{-39} g cm^2)]

Electronic Files
Updated version of the database in ASCII form (BURCAT.THR), is available for free downloading from:
ftp://ftp.technion.ac.il/pub/supported/aetdd/thermodynamics.
The site is mirrored daily by:
http://garfield.chem.elte.hu/Burcat/burcat.html
Transfer the file to your computer using download, or browse through it with your web browser.

Two table generator programs CAP and CAPOLD written by B. McBride are included, to enable generation of thermodynamic properties from the given nine term and seven term polynomials, respectively. The tables generated provide values of C_p, S, H_T-H_{298}, -(G_T-H_{298})/T and H_T as a function of T. Values of $\Delta_f H_T$ and log K_c can be added at any temperature interval within the polynomial's given limit.

A special file called THERM. DAT contains the file burcat.thr stripped of all comments, to be used with

CHEMKIN and similar programs.

Finally an XML version of the main database (Table 4) is included for the researcher's convenience.

The present database is free for use for non-commercial purposes on condition that proper quotation is given to its source. The database cannot be used for commercial purposes without a written agreement from the authors.

Journal Abbreviations found in the Database Tables
JCP = *J. Chem. Phys.*
JOC = *J. Org. Chem.*
JPC = J. Phys. Chem.
JPC A = *J. Phys Chem. A*
JPCRD= *J. Phys. Chem. Ref. Data*
JTC= *J. Theoret. Chem.*

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