

# IUPAC Critical Evaluation of Thermochemical Properties of Selected Radicals. Part I

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This is the first part of a series of articles reporting critically evaluated thermochemical properties of selected free radicals. The present article contains datasheets for 11 radicals: CH, CH<sub>2</sub>(triplet), CH<sub>2</sub>(singlet), CH<sub>3</sub>, CH<sub>2</sub>OH, CH<sub>3</sub>O, CH<sub>3</sub>CO, C<sub>2</sub>H<sub>5</sub>O, C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>, OH, and NH<sub>2</sub>. The thermochemical properties discussed are the enthalpy of formation, as well as the heat capacity, integrated heat capacity, and entropy of the radicals. One distinguishing feature of the present evaluation is the systematic utilization of available kinetic, spectroscopic and ion thermochemical data as well as high-level theoretical results. © 2005 American Institute of Physics. [DOI: 10.1063/1.1724828]

Key words: critical evaluation; enthalpy of formation; free radicals; thermochemical properties.

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## 1. Introduction

### 1.1. General Introduction

Knowledge of accurate thermochemical properties of free radicals is of great importance in many branches of chemistry, in particular atmospheric<sup>1</sup> and combustion<sup>2</sup> modeling. Thermochemical kinetic estimations sometimes provide the only possibility for obtaining rate coefficients and branching ratios for reactions of short-lived intermediates such as free radicals.

Thermodynamic quantities for stable molecules are relatively well established and reliable values are available in a number of compilations<sup>3–9</sup> (see also Table 3, *vide infra*). Enthalpies of formation for stable molecules are typically obtained from calorimetric determinations, while heat capacities and entropies are derived from the results of spectroscopic measurements. The situation is not nearly as favorable for free radicals. For free radicals and other short-lived intermediates, direct calorimetric measurements are (in most cases) not possible, while spectroscopic investigations require more skill and sophisticated instrumentation. Consequently, thermochemical data for a number of free radicals are still uncertain.

In addition, the ability of quantum chemistry to predict thermochemical properties accurately for radicals is a rapidly changing arena. Computational chemistry has made great advances in predictability, although the open-shell and excited-state aspects that are normally associated with radicals still present significant challenges. However, a solid basis of thermochemistry must now be understood to include the best combination of experimental and computational thermochemistry.

In Table 1, enthalpies of formation are given for a few-

TABLE 1. Enthalpies of formation ( $\text{kJ mol}^{-1}$ ) for selected free radicals at  $T(\text{K})=298.15$ 

Radical	McMillen and Golden <sup>10</sup> (1982)	Gurvich <i>et al.</i> <sup>3,4</sup> (1991)	Berkowitz <i>et al.</i> <sup>11</sup> (1994)	Tsang <sup>12</sup> (1996)	NIST CCCBDB <sup>13</sup> (1999)	Kerr and Stocker <sup>14</sup> (2001–2002)	JPL <sup>15</sup> (2003)
$\cdot\text{CH}_3$	146.9±0.6	146.3±0.5	146.4±0.4	147±1	146.3±0.5	146.4±0.4	146.7±0.3
$\text{CH}\equiv\text{C}\cdot$	565±4	568.5±5.0	565.3±2.9		568.5±5.0	566.1±2.9	565.3±2.9
$\text{CH}_2=\text{C}\cdot\text{H}$	294.6±8.4	260±10	299.6±3.3	299±5	299±5	300.0±3.4	299±5
$\text{CH}_3\text{C}\cdot\text{H}_2$	108.4±4.2	107±6	120.9±1.7	119±2	107±6	120.9±1.6	120.9±1.7
$\text{CH}\equiv\text{CC}\cdot\text{H}_2$	340.6±8.4			339±4	339±4	340.6±8.4	
$\text{CH}_2=\text{CHC}\cdot\text{H}_2$	163.6±6.3		170.7±8.8	171±3	171±3	170.7±8.8	166.1±4.3
$(\text{CH}_3)_2\text{C}\cdot\text{H}$	76.2±4.2		90.0±1.7	88±2	76.2	86.6±2.0	86.6±2.0
$(\text{CH}_3)_3\text{C}\cdot$	36.4±4.2		51.5±1.7	48±3	39.3	51.8±1.3	
$\text{C}_6\text{H}_5\text{C}\cdot\text{H}_2$	200±6.3		202.5±6.3	207±4		208.0±2.5	
$\cdot\text{CN}$	435±8	440±5	441.4±4.6		440.3±5.0	441.4±4.6	440±5
$\text{CH}_3\text{C}\cdot=\text{O}$	-24.3±1.7		-10.0±1.3	-12±3	-12±3	-10.0±1.2	-10.0±1.2
$\cdot\text{CH}_2\text{OH}$	-25.9±6.3		-17.1±3.3	-9±4	-17.8±2.6	-17.8±1.3	-11.5±1.3
$\cdot\text{OH}$	39.5	39.4±0.2	39.3±0.2		39.3±0.2	39.3	37.2±0.4
$\cdot\text{NH}_2$	185.4±4.6		188.7±1.3		190.4±6.3	188.7±1.3	186±1
$\cdot\text{SH}$	140.6±4.6	140.4±3.5	143.0±2.9		140.4±3.5	143.0±2.8	142.8±2.9

selected free radicals, taken from seven widely used compilations of the last 2 decades. The compilations by McMillen and Golden<sup>10</sup> and by Tsang<sup>12</sup> evaluate results obtained primarily from halogenation kinetics and from shock tube or other kinetic measurements, respectively. The review of Berkowitz *et al.*<sup>11</sup> derives bond dissociation energies and enthalpies of formation of radicals from ion thermochemical cycles and from chemical kinetics measurements. The work of Gurvich *et al.*<sup>3,4</sup> presents the evaluation of measurements made with various experimental techniques. The remaining compilations select their enthalpy of formation usually from previously published primary evaluations, that is, from evaluations that develop a recommended value from original studies. The free radicals presented in Table 1 are those for which the most data are found in the listed compilations.

A comparison of the data, given in these compilations, shows that the reported enthalpies of formation did not change significantly with time for some of the free radicals (e.g.  $\text{CH}_3$ ,  $\text{C}_3\text{H}_3$ ,  $\text{NH}_2$ , and  $\text{SH}$ ). However, for most other radicals, a considerable change occurred regarding the best value for the enthalpy of formation. [For example, consider the data reported for the simple alkyl radicals  $\text{CH}_3\text{CH}_2$ ,  $(\text{CH}_3)_2\text{CH}$  and  $(\text{CH}_3)_3\text{C}$ .] Typically, a significant increase in the enthalpy of formation on the order of  $10 \text{ kJ mol}^{-1}$  may be seen for a number of radicals presented in Table 1. Nevertheless, data reported in the compilations published in the last few years seem to have converged to some common values. All this suggests that more than twenty years after the publication of the comprehensive review of McMillen and Golden,<sup>10</sup> a new critical evaluation of available thermochemical data becomes timely.

## 1.2. Establishment of the Task Group and Organization of the Project

The idea of initiating a project dealing with the compilation and critical evaluation of thermodynamic properties of free radicals, both originating from experiment and computations, dates back to the 40<sup>th</sup> IUPAC General Assembly held in Berlin in 1999. At the discussions of the I.4 Commission on Chemical Kinetics, the participants came to the conclusion that accurate and reliable thermodynamic data, which are required in modeling of atmospheric processes, combustion and other complex chemical systems, are not available for many important free radicals, literature data are often contradictory, and in some cases they are based on estimations or depend on a single determination made several years ago using indirect methods. It was also concluded that, due to the progress made in developing new experimental techniques, thermochemical properties are becoming increasingly more reliable. In addition, theoretical studies using state-of-the-art quantum chemical techniques have become able to supply data with remarkable accuracy and with uncertainty that is comparable or even better than the experimental uncertainty. This analysis of the state of affairs motivated the I.4 Commission on Chemical Kinetics to suggest a study with the goal of compiling and critically evaluating thermodynamic quantities for free radicals. The idea was supported by the I.5 Commission on Molecular Structure and Spectroscopy. Dr. Michel J. Rossi, chairman of Commission I.4, asked Dr. Tibor Bérces to organize a Task Group and draft a proposal. As a consequence, a Task Group was set up that consists of the following six experimentalists and seven theoreticians from seven countries:

TABLE 2. List of free radicals and reactive intermediates targeted for evaluation

Hydrocarbon radicals	Other carbon-centered radicals	Oxygen-centered radicals	Miscellaneous radicals
·CH	·CN	·OH	·NH <sub>2</sub>
CH <sub>2</sub> ( <sup>3</sup> B <sub>1</sub> )	CF <sub>2</sub>	CH <sub>3</sub> O·	·NO <sub>3</sub>
CH <sub>2</sub> ( <sup>1</sup> A <sub>1</sub> )	CCl <sub>2</sub>	CH <sub>3</sub> CH <sub>2</sub> O·	·SH/·SD
·CH <sub>3</sub>	HC·=O/DC·=O	C <sub>6</sub> H <sub>5</sub> O·	CH <sub>3</sub> S·
CH≡C·	·CH <sub>2</sub> OH	HOO·	·SSH
CH <sub>2</sub> =C·H	HOC·=O	CH <sub>3</sub> OO·	
CH <sub>3</sub> C·H <sub>2</sub>	CH <sub>3</sub> C·=O		
CH≡CC·H <sub>2</sub>	·CH=C=O		
CH <sub>2</sub> =CHC·H <sub>2</sub>	·CH <sub>2</sub> C(O)H		
(CH <sub>3</sub> ) <sub>2</sub> C·H	CH <sub>3</sub> CH <sub>2</sub> C·=O		
CH <sub>3</sub> CH <sub>2</sub> C·HCH <sub>3</sub>			
(CH <sub>3</sub> ) <sub>3</sub> C·			
·C <sub>6</sub> H <sub>5</sub>			
C <sub>6</sub> H <sub>5</sub> C·H <sub>2</sub>			

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A work program was developed by the Task Group and a project proposal was submitted to the IUPAC Secretariat with the title of "Selected Free Radicals and Critical Intermediates: Thermodynamic Properties from Theory and Experiment." The Physical and Biophysical Chemistry Division and the Project Committee reviewed the proposal and approved the project on May 14, 2001 as one of the Divisional activities. The assigned project number was 2000-013-1-100 with a project lifetime of 2.5 years.

### 1.3. Objectives, Scope, and Work Program of the Task Group

The main objective of this Task Group has been the compilation and critical evaluation of available thermodynamic properties, including the computation of accurate thermochemical data for selected free radicals that are of importance in atmospheric and combustion chemistry. A distinguishing feature of the present evaluation is the systematic

utilization of available kinetic, spectroscopic and ion thermochemical data as well as high-level theoretical results.

The free radicals selected for study are given in Table 2. Species for which datasheets are presented in this publication are given in bold. Datasheets for the rest of the radicals will be published in Parts II and III of this series.

## 2. Thermodynamic Quantities

### 2.1. Fundamental Thermodynamic Quantities

The three fundamental thermodynamic quantities of Gibbs energy ( $G$ , also known as free enthalpy), enthalpy ( $H$ ), and entropy ( $S$ ) are related by the defining equation

$$G = H - TS. \quad (1)$$

In thermochemical calculations, differences of thermodynamic quantities usually occur rather than their absolute values, thus the fundamental relationship for a reaction is

$$\Delta_r G^\circ = \Delta_r H^\circ - T \Delta_r S^\circ. \quad (2)$$

The molar enthalpy change in the reaction ( $\Delta_r H^\circ$ ) is related to the molar internal energy change ( $\Delta_r U^\circ$ ) by the equation

$$\Delta_r H^\circ = \Delta_r U^\circ + \Delta_r(pV), \quad (3)$$

where  $p$ ,  $V$ , and  $T$  are the pressure, molar volume, and temperature, respectively. Using the ideal gas law, the last term in Eq. (3) may be expressed as  $RT\Delta n$ , where  $\Delta n$  designates the change in the mole number in the reaction. At  $T/K=0$

$$\Delta_r G^\circ_0 = \Delta_r H^\circ_0 = \Delta_r U^\circ_0. \quad (4)$$

The Gibbs energy of the reaction is related to the equilibrium constant  $K^\circ_T$ :

$$\Delta_r G^\circ_T = -RT \ln K^\circ_T. \quad (5)$$

The enthalpy change in a reaction may be expressed in terms of the enthalpies of formation for reactants and products

$$\Delta_r H^\circ_T = \sum \Delta_r H^\circ_T(\text{products}) - \sum \Delta_r H^\circ_T(\text{reactants}). \quad (6)$$

The reaction enthalpy may be calculated according to Eq. (6), or it may be computed from the equilibrium constant determined as a function of temperature using the van't Hoff relation. (The enthalpy of formation is itself an enthalpy of reaction for the hypothetical reaction forming the species from its elements in their standard states at standard pressure.)

The change of reaction enthalpy with temperature can be given by

$$\Delta_r H^\circ_{T_2} = \Delta_r H^\circ_{T_1} + \int_{T_1}^{T_2} \Delta_r C^\circ_p(T) dT. \quad (7)$$

The last term in Eq. (7) is the integrated heat capacity or enthalpy increment

$$\int_{T_1}^{T_2} \Delta_r C^\circ_p(T) dT = \sum [H^\circ(T) - H^\circ(0)](\text{products}) - \sum [H^\circ(T) - H^\circ(0)](\text{reactants}), \quad (8)$$

which may either be obtained from experiment or calculated from structural parameters and vibrational frequencies using standard statistical mechanics expressions. In the simplest case, the rigid rotor-harmonic oscillator (RRHO) approximation may be used.<sup>16</sup> However, in case of significant anharmonicity or for species with large amplitude motions (e.g., those containing internal rotors), more refined treatments are required.<sup>17-19</sup>

The reaction entropy

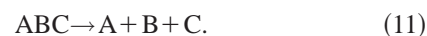
$$\Delta_r S^\circ_T = \sum S^\circ_T(\text{products}) - \sum S^\circ_T(\text{reactants}) \quad (9)$$

may be obtained either from equilibrium measurements as a function of temperature, or it may be calculated from structural parameters and vibrational frequencies using standard statistical mechanics expressions. The RRHO approximation<sup>16</sup> or more refined treatments<sup>17-19</sup> may be utilized. The change of reaction entropy with temperature may be given as

$$\Delta_r S^\circ_{T_2} = \Delta_r S^\circ_{T_1} + \int_{T_1}^{T_2} (1/T) \Delta_r C^\circ_p dT. \quad (10)$$

### 2.2. Dissociation Energies

Atomization energy denotes the energy change in a gas-phase process in which a substance is separated into its constituent atoms in their respective ground state.<sup>20</sup> For a triatomic species ABC, the atomization process is



Within the ideal gas approximation, the atomization enthalpy ( $\Delta_{\text{at}} H^\circ_T$ ) and atomization energy ( $\Delta_{\text{at}} U^\circ_T$ ) are related by

$$\Delta_{\text{at}} H^\circ_T = \Delta_{\text{at}} U^\circ_T + \Delta n RT, \quad (12)$$

where  $\Delta n$  designates the change of the mole number in the atomization process. The atomization energy is related but different from the "bond energy" term, which is sometimes used in qualitative and semiquantitative physical organic chemistry.<sup>20</sup> While these bond energy terms are assigned in such a way that their sum over all bonds corresponds to the atomization energy, the individual bond energies typically correspond to "average" energies over equivalent bonds rather than to actual thermochemical processes describing sequential bond cleavages. Hence, these "bond energies" are not particularly useful in deriving enthalpies of formation of free radicals and other transient intermediates, and they are entirely different from the "bond dissociation energies," which follow a more rigorous thermochemical definition and are described below.

Of particular relevance to this work are the bond dissociation energies ( $\Delta_d U^\circ_T$ ) and enthalpies ( $\Delta_d H^\circ_T$ ), which are defined as the internal energy change and the enthalpy

change, respectively, in a process in which a specific bond is cleaved and the products are formed in their ground states. For the dissociation of the R–X bond, the fragmentation process is



The bond dissociation enthalpy and bond dissociation energy are related by Eq. (14)

$$\Delta_{\text{d}}H^{\circ}_T = \Delta_{\text{d}}U^{\circ}_T + RT. \quad (14)$$

At  $T(\text{K})=0$ ,  $\Delta_{\text{d}}H^{\circ}_0 = \Delta_{\text{d}}U^{\circ}_0$ , and this quantity for the cleavage of the R–X bond will be designated as  $D_0(\text{R–X})$ .  $D_0$  differs from  $D_e$  by the zero-point energy ( $E_{\text{zpe}}$ )

$$D_0(\text{R–X}) = D_e(\text{R–X}) - E_{\text{zpe}}(\text{RX}) + E_{\text{zpe}}(\text{R}) + E_{\text{zpe}}(\text{X}), \quad (15)$$

where  $D_e$  is the bond dissociation energy for the appropriate hypothetical molecule without zero-point energy, and  $E_{\text{zpe}}(\text{X})=0$  if X is an atom.

At finite temperatures, we prefer the use of the bond dissociation enthalpy ( $\Delta_{\text{d}}H^{\circ}_T$ ) which will be designated as  $D_T(\text{R–X})$  for the cleavage of the R–X bond at temperature  $T$ . This quantity is traditionally designated as  $DH^{\circ}_T(\text{R–X})$ , however, here we retain the simpler form. For  $D_T$ , the use of the expression bond energy instead of bond dissociation energy or bond strength is discouraged because it may cause confusion with the bond energy term (see above).

### 2.3. Enthalpies of Formation

The measurement of a bond dissociation energy may result in the determination of the enthalpy of formation for a species provided that the enthalpies of formation are known for the rest of the species involved in the dissociation process. The fundamental relationship for the dissociation process



is

$$D_T(\text{R}_1 - \text{R}_2) = \Delta_{\text{f}}H^{\circ}_T(\text{R}_1) + \Delta_{\text{f}}H^{\circ}_T(\text{R}_2) - \Delta_{\text{f}}H^{\circ}_T(\text{R}_1\text{R}_2), \quad (17)$$

where  $\Delta_{\text{f}}H^{\circ}_T(\text{R}_1)$ ,  $\Delta_{\text{f}}H^{\circ}_T(\text{R}_2)$ , and  $\Delta_{\text{f}}H^{\circ}_T(\text{R}_1\text{R}_2)$  designate the standard enthalpies of formation for  $\text{R}_1$ ,  $\text{R}_2$  and  $\text{R}_1\text{R}_2$ , respectively.

Auxiliary data used in the derivation of thermodynamic quantities in this work are taken from various compilations mentioned in the comments attached to the tables in the datasheets (*vide infra*). However, where possible, thermodynamic quantities for atoms and simple molecules are taken from *CODATA Key Values for Thermodynamics*,<sup>5</sup> and for neutral molecules, they are obtained preferably from the compilation of Gurvich *et al.*<sup>3,4</sup>

### 2.4. Ion Thermochemical Quantities

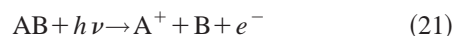
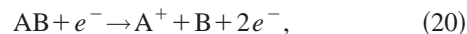
The two basic ion thermochemistry quantities are the ionization energy ( $E_{\text{i}}$ ) and the electron affinity ( $E_{\text{ea}}$ ), which are

related to the energy changes in the electron removal processes of an electron from a neutral species [Eq. (18)] and from an anion [Eq. (19)], respectively:<sup>21,22</sup>



(Note that with this convention stable anions are associated with positive values of electron affinity.) If the transitions occur between the ground vibrational states of neutral species and ions, the energy changes are termed adiabatic ionization energies ( $E_{\text{i,ad}}$ ) and adiabatic detachment energies (or electron affinities) ( $E_{\text{ea,ad}}$ ). Note that  $E_{\text{i,ad}} = \Delta_{\text{r}}U_0(18) = \Delta_{\text{r}}H_0(18)$  and  $E_{\text{ea,ad}} = \Delta_{\text{r}}U_0(19) = \Delta_{\text{r}}H_0(19)$ . As opposed to these adiabatic quantities, vertical ionization energies ( $E_{\text{i,ve}}$ ) and vertical detachment energies (or electron affinities) ( $E_{\text{ea,ve}}$ ) cannot be used in a simple fashion to relate thermochemical quantities of the neutral species AB and its charged counterpart.

Another frequently used ion thermochemistry quantity is the fragment appearance energy ( $E_{\text{ap},T}$ ) which is the minimum energy required to form a cationic fragment from a neutral molecule via dissociative ionization. The appearance energy (often called appearance potential in older literature) of cation  $\text{A}^+$  from molecule AB in electron impact or photon impact processes



is designated by  $E_{\text{ap},T}(\text{A}^+/\text{AB})$ . Note that  $E_{\text{ap},0}(\text{A}^+/\text{AB}) = \Delta_{\text{r}}U_0(20,21) = \Delta_{\text{r}}H_0(20,21)$ , but that  $E_{\text{ap},T}(\text{A}^+/\text{AB})$  is not equal either to  $\Delta_{\text{r}}U_T(20,21)$  or to  $\Delta_{\text{r}}H_T(20,21)$  at any  $T$  different from 0 K.<sup>23</sup>

The enthalpy change of reaction (22)



is traditionally called the proton affinity of molecule B ( $\Delta_{\text{pa}}H_T(\text{B})$ ), while the Gibbs energy change of reaction (22) is the gas-phase basicity of molecule B ( $\Delta_{\text{pa}}G_T(\text{B})$ ). The proton affinity of anion  $\text{A}^-$ , expressed either as the enthalpy change or the Gibbs energy change of reaction (23), is known as the gas phase acidity of molecule HA ( $\Delta_{\text{acid}}H_T(\text{HA})$ ) or ( $\Delta_{\text{acid}}G_T(\text{HA})$ )



The treatment of ion thermochemical quantities associated with processes producing or consuming electrons (e.g., ionization energy, electron affinity, and appearance energy) may become problematic because two different conventions are often adopted in the definition of the thermodynamics of the electron.<sup>24</sup>

In the “electron convention” (or “thermal electron convention”) the standard reference state of the electron is defined in the same way as for the elements, i.e., while the enthalpy of formation and the Gibbs energy of formation are defined to be zero at all temperatures, the integrated heat capacity is  $(5/2)RT$  or  $6.197 \text{ kJ mol}^{-1}$  at  $T/\text{K}=298.15$ , cal-

culated using classical Boltzmann statistics for an ideal gas. (Note that Bartmess<sup>24</sup> has recently pointed out that using quantum Fermi–Dirac statistics, the proper integrated heat capacity should be 3.145 kJ mol<sup>-1</sup> at  $T/K=298.15$ .) The “electron convention” is adopted, for example, in the NIST-JANAF tables<sup>7</sup> and in the compilation of Gurvich *et al.*<sup>3,4</sup>

In the “ion convention” (or “stationary electron convention”) the enthalpy of formation of the electron is similarly defined to be zero at all temperatures, but the integrated heat capacity [ $H^\circ(T) - H^\circ(0)$ ] is also defined to be zero at all temperatures (hence “stationary”). The “ion convention” is used in virtually all papers dealing with ion thermochemistry.

As a result of the different definitions, at  $T/K=298.15$  the enthalpies of formation of cations are higher and those of anions are lower by 6.197 kJ mol<sup>-1</sup> in the electron convention than in the ion convention, although they are the same at  $T/K=0$ . In practice, either convention can be used as long as enthalpies of formation of charged species derived on the basis of different conventions are not combined without proper conversion. In this work the ion (stationary electron) convention is adopted.

### 3. Sources of Information

In this section, the major methods used to determine thermochemical quantities are reviewed. For more detailed information, reference is made to the appropriate literature.

#### 3.1. Thermochemical Data from Kinetics Studies

The kinetic approach of determining the enthalpy of formation for a radical (or any other species) is based on the principle of detailed balance, which asserts that at equilibrium the specific rate of every elementary process is exactly equal to the specific rate of its reverse process. From this it follows that a correlation exists between the equilibrium constant  $K$  of the reversible reaction in which the particular radical participates and the rate coefficients of the elementary reactions in the forward ( $k_f$ ) and in the reverse ( $k_r$ ) direction:

$$K = k_f/k_r. \quad (24)$$

If  $k_f$  and  $k_r$  (expressed in molar units) can be measured accurately as a function of temperature in an appropriate wide temperature range, the Arrhenius activation energies  $E_{a,f}$  and  $E_{a,r}$  are obtained in the usual way and the reaction enthalpy is established at the midtemperature of the experiments:

$$\Delta_r H^\circ_T = (E_{a,f} - E_{a,r}) + RT. \quad (25)$$

From the reaction enthalpy, the enthalpy of formation of the particular radical and the appropriate bond dissociation energies are obtained using fundamental thermodynamic relationships as described in Sec. 2.1. (Note that in this approach,  $\Delta_r H^\circ_T/R$  corresponds to the negative of the slope of the plot of  $\ln K^\circ_T$  versus  $1/T$ .) This procedure is known as the second law method for deriving thermochemical data from kinetic studies.

If  $k_f$  and  $k_r$  are available from kinetic studies only at a single temperature or in a limited temperature range, experiment provides  $K_T$  and, by means of Eq. (5),  $\Delta_r G^\circ_T$  at one temperature. However, if  $\Delta_r S^\circ_T$  can be calculated from the entropies of reactants and products available in the literature, the reaction enthalpy  $\Delta_r H^\circ_T$  and from this the required enthalpy of formation of the particular radical as well as the appropriate bond dissociation energies are easily derived using the relationships given in Sec. 2.1. This is the third law method for obtaining thermochemical data from kinetic studies. The third law method may provide more accurate enthalpies of formation for radicals than the second law method if accurate reaction entropy,  $\Delta_r S^\circ_T$ , can be provided. This is usually the case if a relatively small radical is considered for which reliable structural data and vibrational frequencies are available from experiment and/or *ab initio* calculations providing the basis for accurate determination of the required entropies.

The determination of the equilibrium constant by kinetic methods requires the accurate knowledge of rate coefficients for the reversible reaction in the forward and reverse direction (see Eq. (24)). This is, however, sometimes not the case. Therefore, in earlier studies often assumptions were made. Bond fission reactions, like reaction (16), were frequently used to derive bond dissociation energies (second law determination) by estimating the activation energy for the radical combination reaction. It is generally accepted that free radical recombination reactions have small negative activation energies, depending on the molecular complexity of the radicals involved.

Various kinetic techniques have been developed for the determination of bond dissociation energies and enthalpies of formation of free radicals. Detailed description of these techniques can be found in the literature.<sup>10–12</sup> Here we mention only those kinetic studies of equilibria which have supplied most of the recent thermochemical information for free radicals. The most important types of kinetic studies in this context are as follows.

(i) Thermal decomposition and radical combination studies. Single pulse shock tube studies have supplied a significant part of the determinations of the rate expressions for bond cleavage processes. These, combined with lower-temperature data for radical recombination, gave the value of equilibrium constants from which a number of enthalpies of formation of radicals could be derived. A special case of this type of kinetic studies is the investigation of radical decomposition and the reverse radical/atom addition to an unsaturated bond.

(ii) Time-resolved kinetic studies of abstraction reactions in the forward and reverse direction. A large number of studies have obtained radical thermochemistry from the direct investigation of the kinetics of the



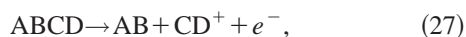
equilibria, where X indicates a halogen atom, in most cases Br atom and sometimes Cl or I. These time resolved kinetic

equilibrium studies may be considered as the continuation of the iodination or bromination technique originally introduced and reviewed by Golden and Benson.<sup>25</sup>

### 3.2. Thermochemical Data from Ion Studies

While kinetic measurements utilize the second and/or third law of thermodynamics to derive thermochemical values, thermochemical cycles (whether ion cycles or otherwise) rely on the first law of thermodynamics. The most frequently used ion thermochemical cycles are known, in their simplest variants, as the “positive ion cycle” and the “negative ion cycle.” They are described in significant detail elsewhere<sup>11,22,23</sup> and hence only a brief summary is given below.

The simplest positive ion cycle that leads to the AB–CD bond dissociation energy of some molecule ABCD involves the following three reactions:



The enthalpy of reaction (27) at  $T/K=0$  corresponds to the  $T/K=0$  appearance energy of the  $\text{CD}^+$  fragment from ABCD,  $\Delta_r H^\circ_0(27) \equiv E_{\text{ap},0}(\text{CD}^+/\text{ABCD})$ . This appearance energy can be obtained, for example, from photoionization mass spectrometric experiments. The enthalpy of reaction (28) at 0 K corresponds to the adiabatic ionization energy of fragment CD (which is usually a radical),  $\Delta_r H^\circ_0(28) \equiv E_{\text{i,ad}}(\text{CD})$ , obtainable from photoelectron or photoionization mass spectrometric studies of radicals, for example. The enthalpy of the third reaction corresponds to the desired bond dissociation energy,  $\Delta_r H^\circ_0(29) \equiv D_0(\text{AB}-\text{CD})$ . By virtue of  $\Delta_r H^\circ(29) = \Delta_r H^\circ(27) - \Delta_r H^\circ(28)$ , it follows that  $D_0(\text{AB}-\text{CD}) = E_{\text{ap},0}(\text{CD}^+/\text{ABCD}) - E_{\text{i,ad}}(\text{CD})$ . Hence, in the positive ion cycle, the bond dissociation energy can be determined as a difference of two measured quantities, one usually for a stable species and the other for a radical. At least in principle, both measurements can be performed in the same laboratory and even on the same apparatus. The experimental challenges are typically centered around the clean *in situ* preparation of the radicals of interest, and sometimes also around the proper interpretation of the spectral data, particularly in determining  $E_{\text{ap},0}$ . While electron-impact methods are easier to apply, they are notorious for producing results that have high uncertainty limits. On the other hand, properly executed and well-interpreted photoionization-type and photoelectron-type measurements can produce  $D_0(\text{AB}-\text{CD})$  with accuracies of  $\pm(1-2)$  kJ mol<sup>-1</sup>, and in selected cases  $\pm 0.5$  kJ mol<sup>-1</sup> or even better.

The simplest negative ion cycle that leads to the AB–CD bond dissociation energy involves



together with reactions (28) and (29). Note that  $\Delta_r H^\circ(30) + \Delta_r H^\circ(31) = \Delta_r H^\circ(27)$  and that at 0 K  $\Delta_r H^\circ_0(30) + \Delta_r H^\circ_0(31) \equiv E_{\text{ap},0}(\text{CD}^+/\text{ABCD})$ . Process (30) is known as heterolytic bond dissociation or ion-pair formation, and in a limited number of cases (because its partial cross section is usually extremely low) the determination of  $\Delta_r H^\circ_0(30)$  is accessible to photoionization-type experiments. The enthalpy of reaction (31) at  $T/K=0$  corresponds to the electron affinity of AB,  $\Delta_r H^\circ_0(31) \equiv E_{\text{ea,ad}}(\text{AB})$ , obtainable from photoelectron spectroscopic measurements of negative ions, for example. The negative ion cycle is most readily applied to the case where CD is simply a hydrogen atom. Replacing CD with H and AB with R, the pertinent reactions acquire the form



In this case, the enthalpy/Gibbs energy of reaction (32) corresponds to the gas-phase acidity of RH,  $\Delta_{\text{acid}}H_T(\text{RH})$ , or  $\Delta_{\text{acid}}G_T(\text{RH})$ , which can be determined via various experimental techniques, most frequently at  $T/K=298.15$ . By virtue of  $\Delta_r H^\circ(35) = \Delta_r H^\circ(32) + \Delta_r H^\circ(33) - \Delta_r H^\circ(34)$ , it follows that  $D_0(\text{R}-\text{H}) = \Delta_{\text{acid}}H^\circ_0(\text{RH}) + E_{\text{ea,ad}}(\text{R}) - E_{\text{i}}(\text{H})$ . Hence, in the negative ion cycle, as applied to hydrogen bond dissociation energies,  $D_0(\text{R}-\text{H})$  can be determined (with necessary conversion between Gibbs energy and enthalpy and between temperatures) from two measured quantities, the gas-phase acidity of RH and the electron affinity of R. A slight disadvantage of the approach that combines gas-phase acidity and electron affinity is that it is limited to dissociation energies of bonds involving hydrogen. Thus, the determination of gas-phase acidities is somewhat less accurate than that of typical photoionization-type experiments employed in determining electron affinities. Nevertheless, well executed and interpreted experiments can produce  $D_0(\text{R}-\text{H})$  values with accuracies in the range of  $\pm(1-4)$  kJ mol<sup>-1</sup>. In a limited number of cases, where nature makes ion-pair formation processes accessible to spectroscopic determinations, accuracies as high as  $\pm 1$  cm<sup>-1</sup> (or even better) can be achieved.

The positive ion cycle and the negative ion cycle are often complementary in the sense that bond dissociation energies that are not accessible to one type of ion cycle are accessible to the other and *vice versa*. This relationship is due to the instability of certain negative ions (not all species have stable negative ions) and facile rearrangements of ions during photodissociative processes (which usually produce only the most stable positive ion). A good example is the comparison of the two hydrogen bond dissociation energies in methanol. The C–H bond dissociation energy is readily obtainable via the positive ion cycle, but not via the negative ion cycle because  $\text{CH}_2\text{OH}^-$  appears not to be stable and the H atom on the oxygen side is the acidic hydrogen. In contrast, the O–H



bond dissociation energy is obtainable via the negative ion cycle, but is not readily obtainable from the positive ion cycle (although the ionization energies of both  $\text{CH}_2\text{OH}$  and  $\text{CH}_3\text{O}$  are known, the photodissociative ionization of methanol produces the more stable  $\text{CH}_2\text{OH}^+$ , rather than  $\text{CH}_3\text{O}^+$ ).

### 3.3. Thermochemical Data from Theoretical Studies

In recent years sophisticated and highly efficient techniques have been developed for the solution of the electronic and nuclear motion problems of quantum chemistry<sup>26</sup> applicable for small to medium sized molecules and transient species. These new techniques, coupled with the enormous advances witnessed in computer technology, make possible the theoretical determination of thermochemical quantities with an accuracy matching that of experiment.

The internal energy of molecules and radicals is usually calculated within an adiabatic approximation, i.e., as a sum of the electronic and nuclear motion energies. At  $T/K=0$  the latter is equal to the zero point energy (ZPE), while the former is calculated by an approximate solution of the electronic Schrödinger equation. The success of computational quantum chemistry is based on the ability to simultaneously and systematically converge the quantum chemical description to all appropriate limits. For the electronic structure problem the limits include that of the Hamiltonian, of the  $n$ -particle space, and of the one-particle space.

*Ab initio* determination of the internal energy usually starts with the nonrelativistic Born–Oppenheimer (BO) electronic Hamiltonian, represents the  $n$ -particle space by higher order coupled-cluster wave functions<sup>27,28</sup> and uses Gaussian-type orbitals optimized through well established procedures,<sup>29</sup> yielding a hierarchy of basis sets with good convergence properties. To achieve the desired accuracy of about  $1 \text{ kJ mol}^{-1}$  in the enthalpy of formation it is not sufficient to saturate the one and  $n$ -particle spaces, i.e., to reach the nonrelativistic complete basis set (CBS) full configuration interaction limit; small corrections must also be considered. These corrections include core–valence corrections, as it is usually considerably cheaper to converge the valence-only problem, relativistic contributions, including the spin–orbit correction when needed, and the diagonal BO correction. The ZPE must also be computed accurately since its contribution is usually larger than those of the other corrections mentioned. To that end, the harmonic oscillator approximation, employed in all model chemistries (see below), may not be sufficiently accurate since anharmonic corrections may not be accountable by simple scaling procedures. The anharmonicity problem is especially important when the molecule has low-frequency and very anharmonic vibrational modes.

Several so-called model chemistries exist for refined *ab initio* energetic predictions. One of the most developed systematic efforts is the Gaussian- $n$  series.<sup>30</sup> Although the procedure uses an empirical parameter, the so-called higher-level correction, its average accuracy does not exceed  $\pm 1 \text{ kcal mol}^{-1}$ , the so-called chemical accuracy limit. A

similar approach in common use today is the CBS  $n$  scheme<sup>31</sup> providing comparable accuracy. One of the best black-box model chemistries is the W- $n$  protocol.<sup>32</sup> In principle the W- $n$  methods are able to provide subchemical accuracy. All these procedures are aimed at reaching a converged energetic estimate, the focal point<sup>33</sup> of electronic structure computations.

From the calculated internal energies one can derive the principal thermochemical entities, most importantly the enthalpies of formation. The most straightforward way to the converged *ab initio* determination of enthalpies of formation goes through the converged determination of zero-point corrected atomization energies. While this route is viable for small systems, its accuracy is extremely difficult to be pushed below  $1-2 \text{ kJ mol}^{-1}$ .<sup>34</sup> For systems with several atoms a more efficient computational route is the application of appropriate reaction schemes (preferably conserving the number of electron pairs), which offer distinct advantages through favorable error cancellation(s).

Further thermochemical quantities, including temperature-dependent entropies and heat capacities, can also be determined straightforwardly through the RRHO approximation to the nuclear motion problem. Nevertheless, if higher precision is required one has to resort to the direct summation technique for the determination of partition functions. While this is possible for triatomic species,<sup>35</sup> this fully computational approach to supplementary thermochemical quantities has not been pursued actively for larger systems.

## 4. Guide to the Datasheets

### 4.1. Construction of the Datasheets

Each datasheet essentially consists of two parts. The first part details the critical evaluation of published experimental and theoretical data on the enthalpy of formation for the given free radical. The central portion of this part is a table of the enthalpy of formation determinations carried out since the publication of the last comprehensive critical review by McMillen and Golden<sup>10</sup> in 1982. The table is supplemented by detailed comments describing the method of determination, the original measured data on which the particular determinations are based, and the auxiliary data used in the derivation or rederivation of the final results.

At the end of this part, a preferred value of the enthalpy of formation is given, together with the associated overall uncertainty. This is supplemented by comments justifying the selection of the preferred value. The given uncertainty represents the expected 95% confidence limit.

In the selection of the preferred value weighted averages had to be calculated. The weighted average  $\mu$  of a list of  $n$  values  $x_i$ , ( $i=1, \dots, n$ ), where each value has an associated uncertainty  $u_i$ ,  $i=1, \dots, n$ , is obtained from the expression

$$\mu = \frac{\sum_{i=1, \dots, n} (x_i / u_i^2)}{\sum_{i=1, \dots, n} (1 / u_i^2)}. \quad (36)$$

The variance  $s_\mu$  of  $\mu$  is then

TABLE 3. Auxiliary thermodynamic values (kJ mol<sup>-1</sup>)

Species	$\Delta_f H^\circ(298.15 \text{ K})$	$\Delta_f H^\circ(0 \text{ K})$	$H^\circ(298.15 \text{ K}) - H^\circ(0 \text{ K})$	Reference
C (graphite)	0	0	1.050 ± 0.020	5
H <sub>2</sub>	0	0	8.468 ± 0.001	5
O <sub>2</sub>	0	0	8.680 ± 0.002	5
N <sub>2</sub>	0	0	8.670 ± 0.001	5
F <sub>2</sub>	0	0	8.825 ± 0.001	5
Cl <sub>2</sub>	0	0	9.181 ± 0.001	5
C	716.68 ± 0.45	711.194 ± 0.45	6.536 ± 0.001	5
H	217.998 ± 0.006	216.035 ± 0.006	6.197 ± 0.001	5
O	249.180 ± 0.100	246.795 ± 0.100	6.725 ± 0.001	5
N	472.68 ± 0.40	470.818 ± 0.40	6.197 ± 0.001	5
F	79.38 ± 0.30	77.27 ± 0.30	6.518 ± 0.001	5
Cl	121.301 ± 0.008	119.620 ± 0.008	6.272 ± 0.001	5
CH <sub>4</sub>	-74.60 ± 0.30	-66.630 ± 0.30	10.016	3, 4
CH <sub>3</sub> I	15.5 ± 0.8			37
CH <sub>2</sub> O	-108.7 ± 0.5	-104.862 ± 0.5	10.020	3, 4
CH <sub>2</sub> CO	-47.7 ± 1.6	-44.508 ± 1.6	11.796	39, 40
CH <sub>3</sub> C(O)H	-165.8 ± 0.4		12.732	37, 38
CH <sub>3</sub> OH	-201.0 ± 0.60	-190.115 ± 0.60	11.441	3, 4
CH <sub>3</sub> CH <sub>2</sub> OH	-234.8 ± 0.5	-217.082 ± 0.5	14.126	3, 4
CO	-110.53 ± 0.17	-113.81 ± 0.17	8.671 ± 0.001	5
H <sub>2</sub> O	-241.826 ± 0.040	-283.923 ± 0.040	9.905 ± 0.005	5
H <sub>2</sub> O <sub>2</sub>	-135.88 ± 0.22	-129.890 ± 0.22	11.158	3, 4
NH <sub>3</sub>	-45.94 ± 0.35	-38.946 ± 0.35	10.043 ± 0.010	5

$$s_\mu = \left( \frac{\sum_{i=1, \dots, n} [(x_i - \mu)^2 / u_i^2]}{(n-1) \sum_{i=1, \dots, n} (1/u_i^2)} \right)^{1/2} \quad (37)$$

To obtain the final uncertainty corresponding to 95% confidence limits, we multiply  $s_\mu$  by the appropriate factor  $t$  from the Student distribution

$$u_\mu = t \times s_\mu \quad (38)$$

Next, checking for outliers is carried out. If each  $\text{abs}(x_i - \mu)$  difference is less than the greater of  $u_\mu$  or  $u_i$ , the calculated average and uncertainty is accepted. However, if this is not the case, the uncertainty of the worst offender is enlarged to its  $(x_i - \mu)$  value and a new iteration is started in order to obtain the final average and uncertainty. (Note that this procedure is borrowed from network analysis and it is part of the algorithmic procedure built into Active Thermochemical Tables currently under development at Argonne Laboratory.<sup>36</sup>)

In the second part of the datasheet, structural information, vibrational frequencies, heat capacities, and entropies are given. In this part, no critical data evaluation of the published quantities is carried out. Instead, data that appear to represent the best results available in the literature are presented.

#### 4.2. Rederivations and Recalculations

In a number of cases, a fully documented effort has been made to rederive the published enthalpies of formation using more recent and/or consistent thermodynamic quantities. This effort was primarily directed toward published data that

were relevant to the selection of the final preferred value. The auxiliary enthalpies of formation used in the rederivations are summarized in Table 3.

For the sake of consistency, heat capacity, integrated heat capacity, and entropy values were recalculated for a number of free radicals using the selected structural data and vibrational frequencies. This recalculation was carried out primarily in those cases where either better quality data could be obtained than those published in the literature or a more sophisticated computational procedure in generating the thermal functions was possible.

#### 4.3. Polynomials

The tabular form of thermochemical data is not very convenient for computerized application. In order to facilitate the use of thermochemical quantities, Gordon and McBride<sup>41</sup> have developed during the last four decades the so called NASA polynomials.

For the calculation of the thermochemical properties and generation of their polynomials, the NASA program of McBride and Gordon<sup>41</sup> was used. This program calculates thermochemical properties from partition functions as described by McBride and Gordon<sup>41</sup> and/or in the introduction of the *NIST-JANAF Thermochemical Tables*.<sup>7</sup> The calculations were performed using the most recent version of the program known as PAC99. Details pertinent to the individual calculations are given in the datasheets.

In cases where the thermochemical functions were not recalculated, but were adopted from the literature or other previous compilations (notably Gurvich *et al.*<sup>3,4</sup>), the originally reported values were used for deriving the polynomials using

the PAC99 program. The polynomial representation of thermochemical properties is given in two different forms: (i) the older 7-constant NASA polynomials (usually in the range of 200–6000 K), which are widely used in kinetics and combustion and (ii) the newer 9-constant NASA polynomials (usually in the range 50–5000 K). It may be noted that the 9-constant polynomials can reproduce the original values more accurately by two orders of magnitude than the seven term polynomials. It should also be noted that the NASA polynomials are “pinned” at the  $T/K=298.15$  and thus they reproduce this value exactly. The 7- and 9-constant polynomials have two branches in the range of 200–1000 and 1000–6000 K and both branches yield the same value at 1000 K. For the 9 constant polynomials, where an additional lower branch in the 50–200 K range is presented, the first two branches are fitted to give the same value at 200 K.

The thermochemical properties can be calculated in general with confidence in the fourth and fifth digit in the range of 150–3000 K. This is the range which has been chosen to be shown in our tabulation. However since many engineering problems require the knowledge of data above and below this range, we are providing them—where appropriate—in the form of polynomials.

The seven-constant NASA polynomials can be used to calculate the following functions:

$$\frac{C_p^\circ}{R} = a_1 + a_2T + a_3T^2 + a_4T^3 + a_5T^4, \quad (39)$$

$$\frac{H_T^\circ}{RT} = a_1 + \frac{a_2T}{2} + \frac{a_3T^2}{3} + \frac{a_4T^3}{4} + \frac{a_5T^4}{5} + \frac{a_6}{T}, \quad (40)$$

$$\frac{S_T^\circ}{R} = a_1 \ln T + a_2T + \frac{a_3T^2}{2} + \frac{a_4T^3}{3} + \frac{a_5T^4}{4} + a_7, \quad (41)$$

$$\begin{aligned} \frac{G_T^\circ}{RT} = \frac{H_T^\circ}{RT} - \frac{S_T^\circ}{R} = & a_1(1 - \ln T) - \frac{a_2T}{2} - \frac{a_3T^2}{6} - \frac{a_4T^3}{12} \\ & - \frac{a_5T^4}{20} + \frac{a_6}{T} - a_7. \end{aligned} \quad (42)$$

It should be noted that the value  $H_T^\circ$  obtained from the polynomials is the “engineering enthalpy” defined as  $H_T^\circ = \Delta_f H^\circ(298.15 \text{ K}) + \int_{298}^T C_p^\circ dT$ . However,  $H_T^\circ$  for reactants and products can be combined directly to obtain the reaction enthalpy  $\Delta_r H^\circ(T)$ . Similarly, the  $G^\circ/RT$  functions of the species in a reaction can be used directly to compute the reaction’s equilibrium constant in terms of concentrations through

$$\begin{aligned} K_c = (RT)^{-\Delta\nu} \exp \left( \Delta a_1(\ln T - 1) + \frac{\Delta a_2 T}{2} + \frac{\Delta a_3 T^2}{6} \right. \\ \left. + \frac{\Delta a_4 T^3}{12} + \frac{\Delta a_5 T^4}{20} + \frac{\Delta a_6}{T} + \Delta a_7 \right), \end{aligned} \quad (43)$$

where the change in mole number is  $\Delta\nu = \sum \nu_j$  and the coefficient changes are  $\Delta a_i = \sum \nu_j a_{ij}$ , the summations are over

all the reactant and product species  $j$  with the stoichiometric coefficients  $\nu_j$  taken to be positive for products and negative for reactants.

The 7-constant 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  $H(298.15)/R \equiv \Delta_f H^\circ(298.15)/R$ . This value is not used by most other programs, such as CHEMKIN<sup>42</sup> and therefore does not interfere with their calculations.

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

$$\frac{C_p^\circ}{R} = a_1T^{-2} + a_2T^{-1} + a_3 + a_4T + a_5T^2 + a_6T^3 + a_7T^4, \quad (44)$$

$$\begin{aligned} \frac{H_T^\circ}{RT} = & -a_1T^{-2} + \frac{a_2 \ln T}{T} + a_3 + \frac{a_4T}{2} + \frac{a_5T^2}{3} + \frac{a_6T^3}{4} \\ & + \frac{a_7T^4}{5} + \frac{a_8}{T}, \end{aligned} \quad (45)$$

$$\begin{aligned} \frac{S_T^\circ}{R} = & -\frac{a_1T^{-2}}{2} - a_2T^{-1} + a_3 \ln T + a_4T + \frac{a_5T^2}{2} + \frac{a_6T^3}{3} \\ & + \frac{a_7T^4}{4} + a_9, \end{aligned} \quad (46)$$

and also  $G^\circ/RT$  and  $K_c$ , following a similar design as given above for the seven-term polynomial.

In order to get a better fit of the polynomial to the generated values, a set of values was used at smaller temperature intervals than those listed in our tables.

#### 4.4. Notation

The symbols and terminology used in this paper, including the datasheets, correspond to the recommendations of the International Union of Pure and Applied Chemistry (IUPAC).<sup>43</sup> In this work, all extensive thermodynamic properties are molar quantities, therefore the subscript m for “molar” is omitted in the symbols of extensive quantities; for example, for the standard molar entropy the symbol  $S^\circ(298.15 \text{ K})$  or  $S^\circ_{298}(\text{R})$  is used instead of  $S^\circ_{\text{m}}(298.15 \text{ K})$  or  $S^\circ_{\text{m},298}(\text{R})$ . The subscript 298 refers to 298.15 K throughout this work. For the convenience of the reader, a list of symbols is given. For the spectroscopic nomenclature, the practice of Herzberg<sup>44–47</sup> is followed.

#### List of Symbols

$p, T, V$	pressure, temperature in Kelvin, and volume, respectively
$p^\circ$	standard pressure
$R$	gas constant
$g_i$	statistical weight of the $i$ th electronic state
$\sigma_{\text{ext}}$	external symmetry number

$\sigma_{\text{rot}}$	symmetry number of internal rotation		
$B_0$	rotational constant in the ground vibrational state	$\Delta_{\text{at}}H^\circ_T(\text{X})$	change in the bond-cleavage process that forms ground state products
$I_A, I_B, I_C$	principal moments of inertia		atomization energy defined as the enthalpy change in a gas-phase process in which species X is separated into its constituent atoms in the ground state
$I_r$	reduced moment of inertia for an internal rotation (symmetric top)	$\Delta_f H^\circ(T)$ or $\Delta_f H^\circ_T(\text{X})$	standard molar enthalpy of formation of species X from its constituent elements in their standard reference states at temperature $T$
$V_n$	$n$ -fold barrier to internal rotation, where the effective potential for the internal rotation $V_{\text{ir}}$ is usually represented as $V_{\text{ir}} = \frac{1}{2} \sum V_n (1 - \cos n\phi)$	$\Delta_f U^\circ(T)$ or $\Delta_f U^\circ_T(i)$	change in standard molar internal energy for reaction $i$ at temperature $T$
$\nu_i$	$i$ th vibrational wave number	$\Delta_f H^\circ(T)$ or $\Delta_f H^\circ_T(i)$	change in standard molar enthalpy for reaction $i$ at temperature $T$
$\omega_i$	$i$ th harmonic wave number	$\Delta_f S^\circ(T)$ or $\Delta_f S^\circ_T(i)$	change in standard molar entropy for reaction $i$ at temperature $T$
$\chi_{ij}$ and $\alpha^{A,B,C_j}$	anharmonicity and vibration-rotation constants, respectively	$\Delta_f G^\circ(T)$ or $\Delta_f G^\circ_T(i)$	change in standard molar Gibbs energy for reaction $i$ at temperature $T$
$E_{\text{zpe}}$	zero-point energy		
$E_i(\text{X})$	ionization energy of species X		
$E_{i,\text{ad}}, E_{i,\text{ve}}$	adiabatic and vertical ionization energies, respectively		
$E_{\text{ea}}(\text{X})$	electron affinity or detachment energy of species X		
$E_{\text{ea,ad}}, E_{\text{ea,ve}}$	adiabatic and vertical electron affinities, respectively		
$E_{\text{ap},T}(\text{X}^+/\text{XY})$	$\text{X}^+$ fragment appearance energy from species XY at temperature $T$		
$\Delta_{\text{pa}}H^\circ_T(\text{X})$	proton affinity of species X at temperature $T$		
$\Delta_{\text{pa}}G^\circ_T(\text{B})$	gas-phase basicity of molecule B		
$\Delta_{\text{acid}}H^\circ_T(\text{HA})$ or $\Delta_{\text{acid}}G^\circ_T(\text{HA})$	gas-phase acidity of molecule HA		
$k(T)$	rate coefficient of a chemical reaction at temperature $T$		
$A_i$ and $E_{a,i}$	Arrhenius parameters (i.e. preexponential factor and activation energy, respectively) for reaction $i$		
$k_f(T), k_r(T)$	rate coefficients at temperature $T$ for a stated reversible chemical reaction in the forward and reverse directions, respectively		
$A_f, E_{a,f}$ and $A_r, E_{a,r}$	Arrhenius parameters for a stated reversible reaction in the forward and reverse directions, respectively		
$K(T)$	equilibrium constant for a reaction at temperature $T$		
$C_p^\circ(T)$ or $C_{p,T}^\circ(\text{X})$	standard molar heat capacity of species X at constant pressure $p$ and at temperature $T$		
$S^\circ(T)$ or $S^\circ_T(\text{X})$	standard molar entropy of species X at temperature $T$		
$[H^\circ(T) - H^\circ(0)](\text{X})$	standard molar enthalpy increment (integrated heat capacity) of species X between temperatures $T$ and zero		
$H^\circ_T$	“absolute enthalpy,” usually known as “engineering enthalpy,” at temperature $T$		
$D_T(\text{X}-\text{Y})$	dissociation energy or strength of the X-Y bond defined as the enthalpy		

In the table of literature data for the enthalpy of formation, abbreviations are given to indicate the name of the method used in the particular determination. These are explained at the bottom of the table. Exceptions are the names of the computational methods for which well known abbreviations are adopted (see Table 4).

For a summary of the preferred thermochemical data, see Table 5.

#### 4.5. Standard State

The definition of the standard state corresponds to that published by IUPAC,<sup>48</sup> i.e., the standard state for a pure gaseous substance is that of the substance as a (hypothetical) ideal gas at the standard pressure  $p = p^\circ$ . The conventional value for the standard pressure,  $p^\circ$ , was 1 standard atm (101 325 Pa), and this was used in all older publications. However, IUPAC has recently recommended 1 bar (100 000 Pa) as the value for the standard pressure. The values of  $S^\circ$  are affected by the choice of the standard pressure. The present work adopts the recommended  $p^\circ = 100\,000$  Pa. To determine the value of  $S^\circ(298.15\text{ K})$  conforming to the older standard state of  $p^\circ = 101\,325$  Pa (1 atm), all  $S^\circ(298.15\text{ K})$  given at 100 000 Pa should be decreased by  $0.109\text{ J mol}^{-1}\text{ K}^{-1}$ .

#### 4.6. Units

SI units are typically used, i.e., energies and enthalpies are expressed in  $\text{kJ mol}^{-1}$ , while heat capacities and entropies are given in  $\text{J K}^{-1}\text{ mol}^{-1}$ . Other traditionally used units, like  $\text{kcal mol}^{-1}$ , eV, and  $\text{cm}^{-1}$ , occur occasionally when reference is made to the originally measured/calculated quantities. In these cases conversion is made using the CODATA recommendations,<sup>48</sup> i.e.,  $1\text{ cal} = 4.184\text{ J}$  and  $1\text{ eV} = 96.4853\text{ kJ mol}^{-1}$ .

TABLE 4. Glossary of computational terms

<i>ab initio</i>	Latin for “from first-principles” or “from scratch”
(aug-)cc-p(C)VnZ	Correlation-consistent (cc) basis sets including diffuse (aug) and core correlation (C) functions
BAC	Bond additivity correction
Born–Oppenheimer approximation	Separation of the nuclear and electronic motion; the nuclei are moving in a potential defined as the electronic energy along the nuclear coordinates
CASSCF	Complete active space SCF; generalization of the one-determinant (Hartree–Fock) wave function which includes several determinants constructed by all possible occupation of the active orbitals
CBS	Complete basis set (limit)
CBS-4, CBS-q, CBS-Q and variants	Complete basis set- <i>n</i> model chemistries
CCSD(T)	Coupled cluster theory with all single and double substitutions and including a perturbative estimate of triples
DFT	Density functional theory
FCI	Full configuration interaction
G1, G2, G3, and variants	Gaussian- <i>n</i> model chemistries
GTO	Gaussian-type orbital
Hamiltonian	Operator employed in the Schrödinger equation
Hartree–Fock method	Simplest level of <i>ab initio</i> electronic structure theory built upon the independent particle approximation. Sometimes called self-consistent-field (SCF) approximation
HO	Harmonic oscillator
HOMO	Highest occupied molecular orbital
MP <i>n</i>	<i>n</i> th-order Møller–Plesset perturbation theory
Potential energy surface (PES)	Defines the molecular energies as a function of geometrical variables
PT	Perturbation theory
RRHO	Rigid rotor harmonic oscillator approximation
W1, W2, and variants	Weizmann- <i>n</i> model chemistries
ZPE	Zero point energy; it is the energy of the lowest energy level corresponding to nuclear motion with respect to the potential energy minimum

#### 4.7. Uncertainties

In this work, recommended values for thermochemical quantities are given together with uncertainties which are intended to represent 95% confidence limits. The use of uncertainties for thermochemical values that correspond to 95% confidence limits (rather than one standard deviation), was originally introduced by Rossini,<sup>49</sup> and subsequently accepted as a standard for thermochemical data by virtually all major thermochemical compilations. (For uncertainty evaluations see also Ref. 50.)

Unfortunately, data published in the literature are often given without thorough error analysis. The uncertainties/error limits are sometimes not given at all, or represent only random errors without taking into account the systematic errors. In addition, thermochemical quantities in the literature

are often obtained by combining the results of different measurements characterized with error limits representing different confidence limits. Finally, even when given by the original authors, the uncertainties are often—without explicitly stating so—intended to represent only 1 s.d., rather than the 95% uncertainty limit (which is roughly equivalent to 2 or more s.d., depending on the number of measurements and the type of uncertainty). Therefore, the uncertainties/error limits given in the literature had to be reestimated/recalculated in many cases, and new uncertainties had to be derived in order to meet the required 95% confidence limits.

In the derivation of thermochemical quantities, auxiliary data are often required, such as enthalpies of formation, heat capacities, and entropies. The uncertainty of the derived quantity depends significantly on the reliability and consis-

TABLE 5. Summary of the preferred thermochemical data

Radical	Formula	$\Delta_f H^\circ(298.15 \text{ K})$ (kJ mol <sup>-1</sup> )	$\Delta_f H^\circ(0 \text{ K})$ (kJ mol <sup>-1</sup> )	$H^\circ(298.15 \text{ K}) - H^\circ(0 \text{ K})$ (kJ mol <sup>-1</sup> )	$C_p^\circ(298.15 \text{ K})$ (J K <sup>-1</sup> mol <sup>-1</sup> )	$S^\circ(298.15 \text{ K})$ (J K <sup>-1</sup> mol <sup>-1</sup> )
Methylidyne	CH ( <sup>2</sup> Π <sub>3/2</sub> )	595.8 ± 0.6	592.5 ± 0.6	8.625	29.175	183.037
Methylene (triplet)	CH <sub>2</sub> ( <sup>3</sup> B <sub>1</sub> )	391.2 ± 1.6	390.7 ± 1.6	10.032	35.130	194.436
Methylene (singlet)	CH <sub>2</sub> ( <sup>1</sup> A <sub>1</sub> )	428.8 ± 1.6	428.3 ± 1.6	9.940	33.781	189.220
Methyl	CH <sub>3</sub> ( <sup>2</sup> A <sub>2</sub> '')	146.7 ± 0.3	150.0 ± 0.3	10.366	38.417	194.008
Benzyl	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> ( <sup>2</sup> B <sub>1</sub> )	208.0 ± 1.7	226.8 ± 1.8	18.178	109.700	318.229
Hydroxymethyl	CH <sub>2</sub> OH ( <sup>2</sup> A [ <sup>2</sup> A''])	-17.0 ± 0.7	-10.7 ± 0.7	11.781	47.401	244.170
Acetyl	CH <sub>3</sub> CO ( <sup>2</sup> A')	-10.3 ± 1.8	-3.6 ± 1.8	12.385	50.785	267.448
Hydroxyl	OH ( <sup>2</sup> Π <sub>3/2</sub> )	37.3 ± 0.3	37.1 ± 0.3	8.813	29.886	183.737
Methoxyl	CH <sub>3</sub> O ( <sup>2</sup> E)	21.0 ± 2.1	28.4 ± 2.1	10.719	42.541	234.278
Ethoxyl	CH <sub>3</sub> CH <sub>2</sub> O ( <sup>2</sup> A'')	-13.6 ± 4.0	-0.2 ± 4.0	14.235	66.321	277.642
Amidogen	NH <sub>2</sub> ( <sup>2</sup> B <sub>1</sub> )	186.2 ± 1.0	189.1 ± 1.0	9.911	33.663	194.868

tency of the auxiliary data used in the derivation. This situation led us to rederive some of the thermochemical quantities published in the literature.

Uncertainties of computed values represent a special case since an error estimation is usually not made in the original literature. However, for certain methods, a systematic analysis of the deviation from experiment of the computed values has been carried out, using relatively large test sets of free radicals. For such theoretical methods, twice the average deviation in the test set is adopted as the uncertainty of the computed values.

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## 6. References (for Sections 1–4)

- R. Atkinson, D. L. Baulch, R. A. Cox, R. F. Hampson, Jr., J. A. Kerr, M. J. Rossi, and J. Troe, *Suppl. V. J. Phys. Chem. Ref. Data* **26**, 521 (1997); *Suppl. VI. J. Phys. Chem. Ref. Data* **26**, 1329 (1997); *Suppl. VII. J. Phys. Chem. Ref. Data* **28**, 191 (1999); *Suppl. VIII. J. Phys. Chem. Ref. Data* **29**, 167 (2000). For more recent updates see (<http://www.iupac-kinetic.ch.cam.ac.uk/>)
- D. L. Baulch, C. J. Cobos, R. A. Cox, P. Frank, G. Hayman, Th. Just, J. A. Kerr, T. Murrells, M. J. Pilling, J. Troe, R. W. Walker, and J. Warnatz, *J. Phys. Chem. Ref. Data* **23**, 847 (1994).
- L. V. Gurvich, I. V. Veyts, and C. B. Alcock, *Thermodynamic Properties of Individual Substances*, 4th ed. (Hemisphere, New York, 1989), Vol. 1.
- L. V. Gurvich, I. V. Veyts, and C. B. Alcock, *Thermodynamic Properties of Individual Substances*, 4th ed. (Hemisphere, New York, 1991), Vol. 2.
- J. D. Cox, D. D. Wagman, and V. A. Medvedev, *CODATA Key Values for Thermodynamics* (Hemisphere, New York, 1989) (see also <http://www.codata.org/codata/databases/key1.html>)
- J. B. Pedley, *Thermochemical Data and Structures of Organic Compounds* (Thermodynamics Research Center, College Station, TX, 1994), Vol. 1.
- NIST-JANAF Thermochemical Tables*, 4th ed., edited by M. W. Chase, Jr., *J. Phys. Chem. Ref. Data, Monograph No. 9* (NIST, Gaithersburg, MD, 1998).
- A. Burcat, *Third Millennium Ideal Gas and Condensed Phase Thermochemical Database for Combustion*, TAE Report No. 867, Technion, Haifa, 2001 (see also <ftp://ftp.technion.ac.il/pub/supported/aetdd/thermodynamics>)
- H. Y. Afeefy, J. F. Liebman, and S. E. Stein, *Neutral Thermochemical Data in NIST Chemistry WebBook, NIST Standard Reference Database Number 69*, edited by P. J. Linstrom and W. G. Mallard (NIST, Gaithersburg, MD, 2001) (see also <http://webbook.nist.gov>).
- D. F. McMillen and D. M. Golden, *Annu. Rev. Phys. Chem.* **33**, 493 (1982).
- J. Berkowitz, G. B. Ellison, and D. Gutman, *J. Phys. Chem.* **98**, 2744 (1994).
- W. Tsang, *Heats of Formation of Organic Free Radicals by Kinetic Methods*, in *Energetics of Organic Free Radicals*, Structure, Energetics and Reactivity in Chemistry (SEARCH) Series, edited by J. A. M. Simoes, A. Greenberg, and J. F. Liebman (Chapman and Hall, London, 1996).
- Computational Chemistry Comparison and Benchmark DataBase (CCCBDB), NIST 1999 (<http://srdata.nist.gov/cccbdb/>).
- A. J. Kerr and D. W. Stocker, *Strengths of Chemical Bonds*, in *CRC Handbook of Chemistry and Physics*, edited by D. Lide, 82nd ed. (CRC Press, Boca Raton, FL, 2001–2002).
- S. P. Sander, R. R. Friedl, D. M. Golden, M. J. Kurylo, R. E. Huie, V. L. Orkin, G. K. Moortgat, A. R. Ravishankara, C. E. Kolb, M. J. Molina, and B. J. Finlayson-Pitts, *JPL Publication 02–25*, NASA and JPL (February 1, 2003).
- K. K. Irikura, *Essential Statistical Thermodynamics*, in *Computational Thermochemistry. Prediction and Estimation of Molecular Thermodynamics*, edited by K. K. Irikura and D. J. Frurip (American Chemical Society, Washington, DC, 1998), pp. 402–418.
- A. L. L. East and L. Radom, *J. Chem. Phys.* **106**, 6655 (1997).
- R. B. McClurg and R. C. Flagan, *J. Chem. Phys.* **106**, 6675 (1997).
- P. Y. Ayala and H. B. Schlegel, *J. Chem. Phys.* **108**, 2314 (1998).
- T. L. Cottrell, *The Strength of the Chemical Bonds* (Butterworths, London, 1954).
- J. C. Traeger and B. M. Kompe, *Thermochemical Data for Free Radicals from Studies of Ions*, in *Energetics of Organic Free Radicals*, edited by J. A. M. Simoes, A. Greenberg, and J. F. Liebman (SEARCH, London, 1996).
- K. M. Ervin, *Chem. Rev.* **101**, 391 (2001).
- See, for example, B. Ruscic, *Res. Adv. Phys. Chem.* **1**, 39 (2000).
- J. E. Bartmess, *J. Phys. Chem.* **98**, 6420 (1994); **99**, 6755E (1995).
- D. M. Golden and S. W. Benson, *Chem. Rev.* **69**, 125 (1969).
- A. G. Császár, W. D. Allen, Y. Yamaguchi, and H. F. Schaefer III, *Ab Initio Determination of Accurate Potential Energy Hypersurfaces for the Ground Electronic States of Molecules*, in *Computational Molecular Spectroscopy*, edited by P. Jensen and P. R. Bunker (Wiley, New York, 2000).
- J. Čížek, *Adv. Chem. Phys.* **14**, 35 (1969).
- Recent Advances in Coupled-Cluster Methods*, edited by R. J. Bartlett (World Scientific, Singapore, 1997).
- T. H. Dunning, Jr., *J. Chem. Phys.* **90**, 1007 (1989).
- J. A. Pople, M. Head-Gordon, D. J. Fox, K. Raghavachari, and L. A. Curtiss, *J. Chem. Phys.* **90**, 5622 (1989).
- G. A. Petersson, A. Bennett, T. G. Tensfeldt, M. A. Al-Laham, W. A. Shirley, and J. Mantzaris, *J. Chem. Phys.* **89**, 2193 (1988).
- J. M. L. Martin and G. de Oliveira, *J. Chem. Phys.* **111**, 1843 (1999); S. Parthiban and J. M. L. Martin, *ibid.* **114**, 6014 (2001); J. M. L. Martin and S. Parthiban, *W1 and W2 theory and their variants: thermochemistry in the kJ/mol accuracy range*, in *Quantum Mechanical Prediction of Thermochemical Data*, edited by J. Cioslowski, Understanding Chemical Reactivity series, Vol. 22 (Kluwer Academic, Dordrecht, 2001), Chap. 2, pp. 31–65.
- A. G. Császár, W. D. Allen, and H. F. Schaefer III, *J. Chem. Phys.* **108**, 9751 (1998).
- T. Helgaker, W. Klopper, A. Halkier, K. L. Bak, P. Jørgensen, and J. Olsen,

- in *Quantum-Mechanical Prediction of Thermochemical Data*, edited by J. Cioslowski (Kluwer, Dordrecht, 2001).
- <sup>35</sup>M. Vidler and J. Tennyson, *J. Chem. Phys.* **113**, 9766 (2000).
- <sup>36</sup>B. Ruscic, R. E. Pinzon, M. L. Morton, B. Wang, A. F. Wagner, G. von Laszewski, S. Bittner, K. A. Amin, S. G. Nijsure, and M. Minkoff, *Active Thermochemical Tables*, Version 1.00 Beta (Argonne National Laboratory, Argonne, IL, 2003); for details see B. Ruscic, R. E. Pinzon, M. L. Morton, G. von Laszewski, S. J. Bittner, S. G. Nijsure, K. A. Amin, M. Minkoff, and A. F. Wagner, *J. Phys. Chem. A* **108**, 9979 (2004); see also B. Ruscic, J. V. Michael, P. C. Redfern, L. A. Curtiss, and K. Raghavachari, *J. Phys. Chem. A* **102**, 10889 (1998), and B. Ruscic, M. Litorja, and R. L. Asher, *ibid.* **103**, 8625 (1999).
- <sup>37</sup>J. B. Pedley and J. Rylance, *Sussex-N. P. L. Computer Analyzed Thermochemical Data: Organic and Organometallic Compounds* (University of Sussex Press, Sussex, 1977).
- <sup>38</sup>C. W. Bauschlicher, Jr., *J. Phys. Chem.* **98**, 2564 (1994).
- <sup>39</sup>R. L. Nuttall, A. H. Laufer, and M. V. Kilday, *J. Chem. Thermodyn.* **3**, 167 (1971).
- <sup>40</sup>J. L. Duncan, A. M. Ferguson, J. Harpper, and K. H. Tonge, *J. Mol. Spectrosc.* **125**, 196 (1987).
- <sup>41</sup>B. J. McBride and S. Gordon, *Computer Program for Calculating and Fitting Thermodynamic Functions*, NASA RP-1271, 1992.
- <sup>42</sup>CHEMKIN IS A PRODUCT OF "REACTION DESIGN."
- <sup>43</sup>I. Mills, T. Cvitas, K. Homann, N. Kallay, and K. Kuchitsu, *Quantities, Units and Symbols in Physical Chemistry*, 2nd ed. (Blackwell Science Ltd., Oxford, U. K., 1993).
- <sup>44</sup>G. Herzberg, *Molecular Spectra and Molecular Structure. I. Spectra of Diatomic Molecules* (Van Nostrand, New York, 1950).
- <sup>45</sup>G. Herzberg, *Molecular Spectra and Molecular Structure. II. Infrared and Raman Spectra of Polyatomic Molecules* (Van Nostrand, New York, 1945).
- <sup>46</sup>G. Herzberg, *Molecular Spectra and Molecular Structure. III. Electronic Spectra of Polyatomic Molecules* (Van Nostrand, New York, 1966).
- <sup>47</sup>K. P. Huber and G. Herzberg, *Molecular Spectra and Molecular Structure. IV. Constants of Diatomic Molecules* (Van Nostrand Reinhold, New York, 1979).
- <sup>48</sup>P. J. Mohr and B. N. Taylor, *J. Phys. Chem. Ref. Data* **28**, 1713 (1999) (see also <http://physics.nist.gov/cuu/Constants/>).
- <sup>49</sup>F. D. Rossini, *J. Res. Natl. Bur. Stand.* **6**, 1 (1931).
- <sup>50</sup>J. A. Manion, *J. Phys. Chem. Ref. Data* **31**, 123 (2002).

## 7. Datasheets

## 7.1. Hydrocarbon Radicals

## 7.1.1. CH Radical

## 7.1.1 Methylidyne Radical

3315-37-5

CH ( ${}^2\Pi_{3/2}$ )	$C_{\infty v}$ ( $\sigma_{\text{ext}}=1$ )
$\Delta_f H^\circ(298.15\text{ K}) = 595.8 \pm 0.6\text{ kJ mol}^{-1}$	$\Delta_f H^\circ(0\text{ K}) = 592.5 \pm 0.6\text{ kJ mol}^{-1}$
$C_p^\circ(298.15\text{ K}) = 29.175\text{ J K}^{-1}\text{ mol}^{-1}$	$H^\circ(298.15\text{ K}) - H^\circ(0\text{ K}) = 8.625\text{ kJ mol}^{-1}$
$S^\circ(298.15\text{ K}) = 183.037\text{ J K}^{-1}\text{ mol}^{-1}$	$p^\circ = 100\,000\text{ Pa (1 bar)}$

## Literature Data for the Enthalpy of Formation at 298.15 K

$\Delta_f H^\circ/\text{kJ mol}^{-1}$	Authors and Reference	Method <sup>a</sup>	Comments
<b>Measurements</b>			
596 <sup>b</sup> ±21	Brewer and Kester (1964) <sup>1</sup>	KE	(1a)
593 <sup>b</sup> ±8	Linevsky (1967) <sup>2</sup>	KE	(1b)
597.3 <sup>b</sup> ±1.3	Herzberg and Johns (1969) <sup>3</sup>	SPEC	(1c)
595.6 <sup>b</sup> ±1.3 <sup>c</sup>	Brooks and Smith (1974) <sup>4</sup>	SPEC	(1d)
596.2 <sup>b</sup> ±1.1	Brzozowski <i>et al.</i> (1976) <sup>5</sup>	SPEC	(1e)
595±13	Jesinger and Squires (1999) <sup>6</sup>	CID	(1f)
<b>Computations</b>			
613.7±9.2 <sup>c</sup>	Zachariah <i>et al.</i> (1996) <sup>7</sup>	BAC-MP4	(1g)
596.6±13 <sup>c</sup>	Curtiss <i>et al.</i> (1998) <sup>8</sup>	CBS-Q	(1h)
590.4±7.9 <sup>c</sup>	Curtiss <i>et al.</i> (1998) <sup>9</sup>	G3	(1i)
596.7±2.5 <sup>c</sup>	Peterson and Dunning (1997) <sup>10</sup>	CCSD(T)	(1j)
595.9±1.9 <sup>c</sup>	Parthiban and Martin (2001) <sup>11</sup>	W2	(1k)
587.7±7.8 <sup>c</sup>	Janoschek and Rossi (2002) <sup>12</sup>	G3MP2B3	(1l)
595.82 <sup>b+0.47/-0.56</sup>	Császár <i>et al.</i> (2002) <sup>13</sup>	FPA	(1m)
<b>Reviews and Evaluations</b>			
596.2±1.1 <sup>c</sup>	Huber and Herzberg (1979) <sup>14</sup>	ST-A	(1n)
595.8	NBS (1982) <sup>15</sup>	TT-U	(1o)
594.1±17.5	JANAF (1985) <sup>16</sup>	CDE	(1p)
597.4±1.3	Gurvich <i>et al.</i> (1991) <sup>17</sup>	CDE	(1q)
597.4±1.3	NIST CCCBDB (1999) <sup>18</sup>	TT-A	(1r)
595.8	CRC HCP (2001) <sup>19</sup>	TT-U	(1s)
596.4±1.2	Kerr and Stocker (2001) <sup>20</sup>	TT-A	(1t)
596.4±1.2	Atkinson <i>et al.</i> (2000) <sup>21</sup>	TT-A	(1u)
597.4±1.3	Burcat (2001) <sup>22</sup>	TT-A	(1v)
597.37±1.3	Sander <i>et al.</i> (2003) <sup>23</sup>	TT-A	(1w)
594.13	NIST WebBook (2003) <sup>24</sup>	TT-A	(1x)

<sup>a</sup>KE: kinetic equilibrium study; SPEC: spectroscopic study; CID: collision induced dynamics; CDE: critical data evaluation; ST-A: annotated tabulation of spectroscopic data; TT-U: unannotated tabulation of thermodynamic data; and TT-A: annotated tabulation of thermodynamic data.

<sup>b</sup>The quoted value was either not given explicitly by the author(s) or it was recalculated using auxiliary thermochemical values that differ from those used by the original authors; see individual comments for additional details.

<sup>c</sup>The uncertainty was either not given explicitly by the original author(s) or it has been modified; see individual comments for further explanations.

## Comments on the Enthalpies of Formation

(1a) A spectroscopic observation of the temperature variation of the intensity of emission from CH in equilibrium with H<sub>2</sub> and graphite, leading to  $D_0(\text{CH}) = 80 \pm 5\text{ kcal mol}^{-1} = 3.5 \pm 0.2\text{ eV}$  ( $335 \pm 21\text{ kJ mol}^{-1}$ ), and also  $\Delta_f H^\circ_0(\text{C}) = 709.5\text{ kJ mol}^{-1}$ . Note that the latter is close to  $\Delta_f H^\circ_0(\text{C}) = 711.194 \pm 0.45\text{ kJ mol}^{-1}$ , which can be obtained from the CODATA recommended<sup>25</sup> values  $\Delta_f H^\circ_{298}(\text{C}) = 716.68 \pm 0.45\text{ kJ mol}^{-1}$ ,  $[H^\circ(298.15\text{ K}) - H^\circ(0\text{ K})](\text{C}) = 6.536 \pm 0.001\text{ kJ mol}^{-1}$ , and  $[H^\circ(298.15\text{ K}) - H^\circ(0\text{ K})]$

(C, graphite) =  $1.050 \pm 0.020\text{ kJ mol}^{-1}$ . The value listed in the table corresponds to the observed  $D_0(\text{CH})$  when coupled with additional auxiliary values as recommended by CODATA,<sup>25</sup>  $\Delta_f H^\circ_{298}(\text{H}) = 217.998 \pm 0.006\text{ kJ mol}^{-1}$ ,  $[H^\circ(298.15\text{ K}) - H^\circ(0\text{ K})](\text{H}) = 6.197 \pm 0.001\text{ kJ mol}^{-1}$ , and  $[H^\circ(298.15\text{ K}) - H^\circ(0\text{ K})](\text{H}_2) = 8.468 \pm 0.001\text{ kJ mol}^{-1}$ , together with  $[H^\circ(298.15\text{ K}) - H^\circ(0\text{ K})](\text{CH}) = 8.625\text{ kJ mol}^{-1}$ , as given by Gurvich *et al.*<sup>17</sup>

(1b) Spectroscopic determination of the concentration of CH in equilibrium with H<sub>2</sub> and graphite (similar to (1a) above),



leading to  $D_0(\text{CH}) = 80.7 \pm 2 \text{ kcal mol}^{-1} = 3.5 \pm 0.1 \text{ eV}$  ( $338 \pm 8 \text{ kJ mol}^{-1}$ ). The value in the table has been derived by using auxiliary thermochemistry given in (1a) above.

(1c) Analysis of lifetimes of observed predissociation (broadening of rotational lines) in  $v=0$  and 1 of  $\tilde{B}^2\Sigma$  states of CH and CD, based on data by the authors<sup>3</sup> and that of Shidei,<sup>26</sup> resulting in  $D_0(\text{CH}) = 27856 \pm 100 \text{ cm}^{-1} = 3.45_4 \pm 0.01_2 \text{ eV}$  ( $333.2 \pm 1.2 \text{ kJ mol}^{-1}$ ). This value supercedes the older estimate of Herzberg<sup>27</sup> of  $D_0(\text{CH}) = 3.47 \text{ eV}$ . The value in the table has been derived by using auxiliary thermochemistry given in (1a) above.

(1d) Further improvement on lifetimes of observed predissociation of  $\tilde{B}^2\Sigma$  state of CH. Their limiting curve of dissociation suggests a slightly higher dissociation energy than that observed by Herzberg and Johns,<sup>3</sup>  $D_0(\text{CH}) \approx 28000 \text{ cm}^{-1} = 3.4_7 \text{ eV}$ . The value in the table has been derived by using auxiliary thermochemistry given in (1a) above and assuming an uncertainty of  $\pm 100 \text{ cm}^{-1}$  for  $D_0(\text{CH})$ .

(1e) Further studies of lifetimes of observed predissociation of  $\tilde{B}^2\Sigma$  state of CH. The limiting curve of dissociation based on new data produces  $D_0(\text{CH}) = 27950 \pm 80 \text{ cm}^{-1} = 3.46_5 \pm 0.01_0 \text{ eV}$ . The value in the table has been derived by using auxiliary thermochemistry given in (1a) above.

(1f) Collision-induced dissociation study of  $\text{CHCl}^-$ ,  $\text{CFCl}^-$ , and  $\text{CCl}_2^-$ . The study reports  $\Delta_f H^\circ_{298}(\text{CH}) = 142.2 \pm 3.2 \text{ kcal mol}^{-1}$ .

(1g) BAC-MP4 *ab initio* computations. The originally quoted uncertainty is  $\pm 4.6 \text{ kJ mol}^{-1}$ , and has been multiplied by factor of 2 to bring it closer to the desired 95% confidence limit.

(1h) CBS-Q value. The reported average absolute deviation of  $1.57 \text{ kcal mol}^{-1}$  was multiplied by 2 to bring it closer to the desired 95% confidence limit. The equivalent CBS-q and CBS-4 enthalpies of formation are  $594.1 \pm 18 \text{ kJ mol}^{-1}$  and  $597.5 \pm 26 \text{ kJ mol}^{-1}$ , where the uncertainties have been obtained in an analogous way.

(1i) G3 *ab initio* calculation. The value listed in the table is converted from  $141.1 \text{ kcal mol}^{-1}$ . The uncertainty quoted in the table corresponds approximately to 95% confidence limits, based on twice the average absolute deviation of  $0.94 \text{ kcal mol}^{-1}$  for the enthalpies in the G2/97 test set, which roughly corresponds to 1 s.d. At the G3(MP2) level of theory<sup>28</sup>  $\Delta_f H^\circ_{298}(\text{CH}) = 588.7 \pm 9.9 \text{ kJ mol}^{-1}$ , where the quoted uncertainty has been derived in a similar fashion as for the G3 value. At the G2 level of theory<sup>29</sup>  $\Delta_f H^\circ_{298}(\text{CH}) = 593.7 \pm 13.1 \text{ kJ mol}^{-1}$ .

(1j) CCSD(T)/cc-pVnZ *ab initio* calculations extrapolated to complete basis set and corrected for core-valence effects produce  $D_0(\text{CH}) = 333.9 \text{ kJ mol}^{-1}$  after inclusion of ZPE. An estimated standard deviation of  $0.3 \text{ kcal mol}^{-1}$  has been quoted by the authors for the sequential set of bond dissociation energies of  $\text{CH}_4$ ; the uncertainty listed in the table corresponds to 2 s.d.

(1k) W2 *ab initio* calculation. The uncertainty quoted in the table corresponds approximately to 95% confidence limits based on twice the average absolute deviation for the W2 test

set of  $0.23 \text{ kcal mol}^{-1}$ , which corresponds roughly to 1 s.d. At the W1 level of theory  $\Delta_f H^\circ_{298}(\text{CH}) = 595.6 \pm 3.1 \text{ kJ mol}^{-1}$ , where the uncertainty has been obtained in an analogous way.

(1l) G3(MP2)//B3LYP *ab initio* calculations for 32 selected free radicals. The uncertainty given in the table corresponds approximately to 95% confidence limits based on twice the quoted average absolute deviation of  $3.9 \text{ kJ mol}^{-1}$  for the calculated set of radicals, which corresponds roughly to 1 s.d. Note that the average absolute deviation for all enthalpies in the G2/97 test set using the same method is very slightly larger.<sup>30</sup>  $4.7 \text{ kJ mol}^{-1}$  [see also (1i) above].

(1m) High-quality *ab initio* study, including higher-order coupled cluster and full CI benchmarks with (aug)-cc-p(C)VnZ,  $n=3, 4, 5, 6$ , extrapolated to CBS limits and very high level corrections, producing  $D_0(\text{CH}) = 334.74^{+0.13}_{-0.34} \text{ kJ mol}^{-1}$ ,  $\Delta_f H^\circ_0(\text{CH}) = 592.48 \text{ b}^{+0.47}_{-0.56} \text{ kJ mol}^{-1}$ , and  $\Delta_f H^\circ_{298}(\text{CH}) = 595.82^{+0.47}_{-0.56} \text{ kJ mol}^{-1}$ , using auxiliary thermochemical values as in (1a) above. (Note that the authors obtain a very slightly different value for the enthalpy at 298.15 K,  $595.93^{+0.47}_{-0.56} \text{ kJ mol}^{-1}$ , because they adopt the enthalpy increment for CH of  $8.730 \text{ kJ mol}^{-1}$  from the JANAF Tables.<sup>16</sup>)

(1n) Huber and Herzberg report  $D_0(\text{CH}) = 3.46_5 \text{ eV}$ , and quote the refinements of Brooks and Smith<sup>4</sup> [(1d) above] and Brzozowski *et al.*<sup>5</sup> [(1e) above] to the original finding of Herzberg and Johns<sup>3</sup> [see (1c) above].

(1o) Critical data evaluation, but does not provide a pedigree of the selected value nor does it quote uncertainties.

(1p) Extensive compilation of thermodynamic data. The CH properties have been last revised in December 1967. The value is based on the outdated older estimate of Herzberg<sup>27</sup> of  $D_0(\text{CH}) = 3.47 \text{ eV}$  [see (1c) above]. There are no changes in the NIST-JANAF Tables.<sup>31</sup>

(1q) Extensive compilation of thermodynamic data. The value is unchanged from the previous (Russian) edition,<sup>32</sup> and is based on the dissociation energy  $D_0(\text{CH}) = 3.454 \pm 0.01 \text{ eV}$  given by Herzberg and Johns<sup>3</sup> [see (1c) above].

(1r) The compilation lists theoretical results at various levels of theory, but also makes a reference to one experimental benchmark. The quoted experimental benchmark value is from Gurvich *et al.*<sup>17</sup> [see (1q) above].

(1s) The tabulation gives a list of compilations as sources, but no specific references for individual species. However, the value appears to correspond to that adopted by the NBS Tables<sup>15</sup> [see (1o) above].

(1t) These authors cite Huber and Herzberg<sup>14</sup> as a source [(1n) above].

(1u) Critical evaluation of atmospherically relevant kinetic data. Their table of enthalpy data lists Kerr and Stocker<sup>20</sup> as the source.

(1v) Thermochemical database for combustion. Burcat quotes Gurvich *et al.*<sup>17</sup> as the source for the enthalpy.

(1w) Critical evaluation of atmospherically relevant kinetic data. The quoted value is from Gurvich *et al.*<sup>17</sup>

(1x) An un-evaluated tabulation of available values, listing the thermochemistry of CH from the NIST-JANAF Tables<sup>31</sup> [see (1p) above].

### Preferred Value of the Enthalpy of Formation

$$\Delta_f H^\circ(298.15 \text{ K}) = 595.8 \pm 0.6 \text{ kJ mol}^{-1}$$

$$\Delta_f H^\circ(0 \text{ K}) = 592.5 \pm 0.6 \text{ kJ mol}^{-1}$$

The best available experimental value,  $\Delta_f H^\circ(\text{CH}, \text{g}, 298.15 \text{ K}) = 596.2 \pm 1.1 \text{ kJ mol}^{-1}$ , was obtained in a spectroscopic study by Brzozowski *et al.*,<sup>5</sup> who improved upon earlier studies by Brooks and Smith<sup>4</sup> and Herzberg and Johns.<sup>3</sup> The value is in good accord with the coarser determinations obtained in older studies of graphite/ $\text{H}_2$  equilibria in a graphite oven<sup>1,2</sup> and with the more recent studies by collision-induced dissociation. The weighted average of all experimental values listed in the table is  $\Delta_f H^\circ(\text{CH}, \text{g}, 298.15 \text{ K}) = 596.3 \pm 1.0 \text{ kJ mol}^{-1}$ , in excellent agreement with the result by Brzozowski *et al.*<sup>5</sup>

Since this is a hydrogen-containing diatomic molecule, one can expect that theory at the highest level will produce reliable values for the dissociation energy. Indeed, the very

high level theoretical study by Császár *et al.*<sup>13</sup> produces a value  $\Delta_f H^\circ(\text{CH}, \text{g}, 298.15 \text{ K}) = 595.82^{+0.47}_{-0.56} \text{ kJ mol}^{-1}$ , which is fully compatible with the experimental values but claims higher accuracy. It should be also noted that the W2 value of Parthiban and Martin<sup>11</sup> is practically the same, albeit with a slightly higher uncertainty than the experiment. Hence, the preferred value corresponds to the theoretical value of Császár *et al.*<sup>13</sup>

The preferred value corresponds to the C–H bond dissociation energy  $D_0(\text{CH}) = 334.74 \pm 0.34 \text{ kJ mol}^{-1}$  ( $338.85 \pm 0.34 \text{ kJ mol}^{-1}$  at 298.15 K), which produces the listed enthalpy when used together with auxiliary thermochemical values as recommended by CODATA<sup>25</sup>  $\Delta_f H^\circ_{298}(\text{H}) = 217.998 \pm 0.006 \text{ kJ mol}^{-1}$ ,  $[H^\circ(298.15 \text{ K}) - H^\circ(0 \text{ K})](\text{H}) = 6.197 \pm 0.001 \text{ kJ mol}^{-1}$ ,  $[H^\circ(298.15 \text{ K}) - H^\circ(0 \text{ K})](\text{C, graphite}) = 1.050 \pm 0.020 \text{ kJ mol}^{-1}$ ,  $\Delta_f H^\circ_{298}(\text{C}) = 716.68 \pm 0.45 \text{ kJ mol}^{-1}$ ,  $[H^\circ(298.15 \text{ K}) - H^\circ(0 \text{ K})](\text{C}) = 6.536 \pm 0.001 \text{ kJ mol}^{-1}$ , and  $[H^\circ(298.15 \text{ K}) - H^\circ(0 \text{ K})](\text{H}_2) = 8.468 \pm 0.001 \text{ kJ mol}^{-1}$ , together with  $[H^\circ(298.15 \text{ K}) - H^\circ(0 \text{ K})](\text{CH}) = 8.625 \text{ kJ mol}^{-1}$  as listed below and given by Gurvich *et al.*<sup>17</sup>

Geometry (distance in Å)<sup>(2a)</sup>

Z matrix		Cartesian coordinates		
		x	y	z
C	C	0.000 000	0.000 000	−0.086 768
H	1 1.1199	0.000 000	0.000 000	1.033 132

Moments of inertia in the electronic ground state<sup>(2b)</sup>

$$I_B = 1.973 \times 10^{-47} \text{ kg m}^2$$

Vibrational wave numbers in the electronic ground state  $[\nu_i / (\text{cm}^{-1})]$ <sup>(2c)</sup>

$$2732.46 (\sigma)$$

Heat capacity  $C_p^\circ$ , entropy  $S^\circ$ , and enthalpy increment  $[H^\circ(T) - H^\circ(0 \text{ K})]$ <sup>(2d),(2e)</sup>

T/K	$C_p^\circ(T)$ ( $\text{JK}^{-1} \text{ mol}^{-1}$ )	$S^\circ(T)$ ( $\text{JK}^{-1} \text{ mol}^{-1}$ )	$[H^\circ(T) - H^\circ(0 \text{ K})]$ ( $\text{kJ mol}^{-1}$ )
150	29.187	162.988	4.301
200	29.179	171.388	5.762
250	29.173	177.899	7.221
298.15	29.175	183.037	8.625
300	29.175	183.217	8.679
350	29.190	187.715	10.138
400	29.225	191.615	11.598
500	29.398	198.152	14.529
600	29.743	203.540	17.484
800	30.860	212.238	23.536
1000	32.272	219.273	29.847
1200	33.748	225.288	36.450
1500	35.825	233.046	46.892
2000	38.551	243.750	65.528
2500	40.342	252.560	85.285
3000	41.491	260.024	105.762

## 7-Constant NASA Polynomial

```

METHYLIDYNE      JUN03 C 1.H 1. 0. 0.G 200.000 6000.000 13.01864 1
0.25209369E+01 0.17653639E-02-0.46147660E-06 0.59289675E-10-0.33474501E-14 2
0.70946769E+05 0.74051829E+01 0.34897583E+01 0.32432160E-03-0.16899751E-05 3
0.31628420E-08-0.14061803E-11 0.70612646E+05 0.20842841E+01 0.71658188E+05 4

```

## 9-Constant NASA Polynomial

```

METHYLIDYNE      IUPAC Task Group on Selected Radicals
2 JUN03 C 1.00H 1.00 0.00 0.00 0.00 0 13.01864 595800.000
200.000 1000.0007 -2.0 -1.0 0.0 1.0 2.0 3.0 4.0 0.0 8625.000
0.223590108D+05-0.342452257D+03 0.554012095D+01-0.581298373D-02 0.798678629D-05
-0.447225508D-08 0.959824993D-12 0.000000000D+00 0.722287398D+05-0.915816739D+01
1000.000 6000.0007 -2.0 -1.0 0.0 1.0 2.0 3.0 4.0 0.0 8625.000
0.205925350D+07-0.539216675D+04 0.785217657D+01-0.794574549D-03 0.175907549D-06
-0.196956391D-10 0.499532673D-15 0.000000000D+00 0.106008917D+06-0.315178740D+02

```

### Comments on Molecular Data, Heat Capacity, Entropy, and Enthalpy Increment

(2a) The geometry reflects<sup>14</sup>  $r_e(\text{CH}) = 1.119_9 \text{ \AA}$ , congruent with  $B_e = 14.457 \text{ cm}^{-1}$ .

(2b) The listed moment of inertia is based on the experimental rotational constant<sup>14</sup>  $B_0 = 14.190 \text{ cm}^{-1}$ .

(2c) The listed vibrational frequency is the fundamental,  $\Delta G_{1/2}$ , corresponding<sup>14</sup> to  $\omega_e = 2858.5 \text{ cm}^{-1}$ ,  $\omega_e x_e = 63.02 \text{ cm}^{-1}$ .

(2d) The heat capacity, entropy, and enthalpy increment values are adopted from Gurvich *et al.*<sup>17</sup> These authors calculated the thermodynamic functions for CH by direct summation over the rovibrational levels of  $\tilde{X}^2\Pi$ ,  $\tilde{a}^4\Sigma^-$ ,  $\tilde{A}^2\Delta$ ,  $\tilde{B}^2\Sigma^-$ , and  $\tilde{C}^2\Sigma^+$  states, terminating appropriately the summations in accord with estimated limiting curves of dissociation for these states. (2e) The standard heat capacity, entropy, and enthalpy increment values reported in the JANAF<sup>16</sup> and NIST-JANAF<sup>31</sup> Thermochemical Tables are  $C_p^\circ(298.15 \text{ K}) = 29.171 \text{ J K}^{-1} \text{ mol}^{-1}$ ,  $S^\circ(298.15 \text{ K}) = 183.040 \text{ J K}^{-1} \text{ mol}^{-1}$ , and  $H^\circ(298.15 \text{ K}) - H^\circ(0 \text{ K}) = 8.730 \text{ kJ mol}^{-1}$ . The *Thermochemical Database for Combustion*<sup>22</sup> lists values in accord with the compilation by Gurvich *et al.*<sup>17</sup> [ $C_p^\circ(298.15 \text{ K}) = 29.175 \text{ J K}^{-1} \text{ mol}^{-1}$  and  $S^\circ(298.15 \text{ K}) = 183.037 \text{ J K}^{-1} \text{ mol}^{-1}$ ]. The values obtained from G3MP2B3 computations<sup>12</sup> are  $C_p^\circ(298.15 \text{ K}) = 29.16 \text{ J K}^{-1} \text{ mol}^{-1}$ ,  $S^\circ(298.15 \text{ K}) = 182.92 \text{ J K}^{-1} \text{ mol}^{-1}$ , and  $H^\circ(298.15 \text{ K}) - H^\circ(0 \text{ K}) = 8.68 \text{ kJ mol}^{-1}$ .

### References

- R. G. Brewer and F. L. Kester, *J. Chem. Phys.* **40**, 812 (1964).
- M. J. Linevsky, *J. Chem. Phys.* **47**, 348 (1967).
- G. Herzberg and J. W. C. Johns, *Astrophys. J.* **158**, 339 (1969).
- N. H. Brooks and W. H. Smith, *Astrophys. J.* **194**, 513 (1974).
- J. Brzozowski, P. Bunker, N. Elander, and P. Erman, *Astrophys. J.* **207**, 414 (1976).
- R. A. Jesinger and R. R. Squires, *Int. J. Mass Spectrom.* **187**, 745 (1999).
- M. R. Zachariah, P. R. Westmoreland, D. R. Burgess, Jr., W. Tsang, and C. F. Melius, *J. Phys. Chem. A* **100**, 8737 (1996); see also D. R. F. Burgess,

Jr., M. R. Zachariah, W. Tsang, and P. R. Westmoreland, *Prog. Energy Combust. Sci.* **21**, 453 (1995).

<sup>8</sup>L. A. Curtiss, K. Raghavachari, P. C. Redfern, and B. B. Stefanov, *J. Chem. Phys.* **108**, 692 (1998).

<sup>9</sup>L. A. Curtiss, K. Raghavachari, P. C. Redfern, V. Rassolov, and J. A. Pople, *J. Chem. Phys.* **109**, 7764 (1998).

<sup>10</sup>K. A. Peterson and T. H. Dunning, Jr., *J. Chem. Phys.* **106**, 4119 (1997).

<sup>11</sup>S. Parthiban and J. M. L. Martin *J. Chem. Phys.* **114**, 6014 (2001).

<sup>12</sup>R. Janoschek and M. J. Rossi, *Int. J. Chem. Kinet.* **34**, 550 (2002).

<sup>13</sup>A. G. Császár, P. G. Szalay, and M. L. Leininger, *Mol. Phys.* **100**, 3879 (2002)

<sup>14</sup>K. P. Huber and G. Herzberg, *Molecular Spectra and Molecular Structure. IV. Constants of Diatomic Molecules* (Van Nostrand, New York, 1979).

<sup>15</sup>D. D. Wagman, W. E. Evans, V. B. Parker, R. H. Schumm, I. Halow, S. M. Bailey, K. L. Churney, and R. L. Nuttall, "The NBS tables of chemical thermodynamic properties," *J. Phys. Chem. Ref. Data* **11**, Suppl. 2 (1982).

<sup>16</sup>M. W. Chase, Jr., C. A. Davies, J. R. Downey, Jr., D. J. Frurip, R. A. McDonald, and A. N. Syverud, *JANAF Thermochemical Tables*, 3rd ed., *J. Phys. Chem. Ref. Data* **14**, Suppl. 1 (1985).

<sup>17</sup>L. V. Gurvich, I. V. Veyts, and C. B. Alcock, *Thermodynamic Properties of Individual Substances*, 4th ed. (Hemisphere, New York, 1991), Vol. 2.

<sup>18</sup>Computational Chemistry Comparison and Benchmark DataBase (CCCBDB), NIST 1999 (see <http://srdata.nist.gov/cccbdb/>)

<sup>19</sup>*Standard Thermodynamic Properties of Chemical Substances*, in *CRC Handbook of Chemistry and Physics*, edited by D. Lide, 82nd ed. (CRC Press, Boca Raton, FL, 2001–2002).

<sup>20</sup>J. A. Kerr and D. W. Stocker, *Strengths of Chemical Bonds*, in *CRC Handbook of Chemistry and Physics*, edited by D. Lide, 82nd ed. (CRC Press, Boca Raton, FL, 2001–2002).

<sup>21</sup>R. Atkinson, D. L. Baulch, R. A. Cox, R. F. Hampson, Jr., J. A. Kerr, M. J. Rossi, and J. Troe, *J. Phys. Chem. Ref. Data* **29**, 167 (2000).

<sup>22</sup>A. Burcat, TAE Report No. 867, Technion, Haifa, 2001 (see also <ftp://ftp.technion.ac.il/pub/supported/aetdd/thermodynamics>)

<sup>23</sup>S. P. Sander, R. R. Friedl, D. M. Golden, M. J. Kurylo, R. E. Huie, V. L. Orkin, G. K. Moortgat, A. R. Ravishankara, C. E. Kolb, M. J. Molina, and B. J. Finlayson-Pitts, JPL Publication 02–25, NASA and JPL, February 1, 2003.

<sup>24</sup>H. Y. Afeefy, J. F. Liebman, and S. E. Stein, *Neutral Thermochemical Data*, in *NIST Chemistry WebBook*, NIST Standard Reference Database Number 69, edited by P. J. Linstrom and W. G. Mallard (NIST, Gaithersburg, MD, 2003) (<http://webbook.nist.gov/>)

<sup>25</sup>J. D. Cox, D. D. Wagman, and V. A. Medvedev, *CODATA Key Values for Thermodynamics* (Hemisphere, New York, 1989) (see also <http://www.codata.org/codata/databases/key1.html>)

- <sup>26</sup>T. Shidei, *Jpn. J. Phys.* **11**, 23 (1936).
- <sup>27</sup>G. Herzberg, *Molecular Spectra and Molecular Structure. I. Spectra of Diatomic Molecules* (Van Nostrand, New York, 1950).
- <sup>28</sup>L. A. Curtiss, P. C. Redfern, K. Raghavachari, V. Rassolov, and J. A. Pople, *J. Chem. Phys.* **110**, 4703 (1999).
- <sup>29</sup>L. A. Curtiss, K. Raghavachari, G. W. Trucks, and J. A. Pople, *J. Chem. Phys.* **94**, 7221 (1991).
- <sup>30</sup>A. G. Baboul, L. A. Curtiss, P. C. Redfern, and K. Raghavachari, *J. Chem. Phys.* **110**, 7650 (1999).
- <sup>31</sup>M. W. Chase, Jr., *NIST-JANAF Thermochemical Tables*, 4th ed., *J. Phys. Chem. Ref. Data Monogr.* **9** (1998).
- <sup>32</sup>V. P. Glushko, L. V. Gurvich, G. A. Bergman, I. V. Veits, V. A. Medvedev, G. A. Khackhuzov, and V. S. Yungman, *Termodinamicheski Svoistva Individual'nikh Veschestv*, 3rd ed. (Nauka, Moscow, 1979).

7.1.2. CH<sub>2</sub> Triplet Radical

## 7.1.2. Methylene Radical (triplet)

2465-56-7

CH <sub>2</sub> ( <sup>3</sup> B <sub>1</sub> )	C <sub>2v</sub> (σ <sub>ext</sub> =2)
Δ <sub>f</sub> H°(298.15 K)=391.2±1.6 kJ mol <sup>-1</sup>	Δ <sub>f</sub> H°(0 K)=390.7±1.6 kJ mol <sup>-1</sup>
C <sup>o</sup> <sub>p</sub> (298.15 K)=35.130 J K <sup>-1</sup> mol <sup>-1</sup>	H°(298.15 K)–H°(0 K)=10.032 kJ mol <sup>-1</sup>
S°(298.15 K)=194.436 J K <sup>-1</sup> mol <sup>-1</sup>	p°=100 000 Pa (1 bar)

Note: For applications where triplet methylene is not equilibrated with singlet methylene, only Δ<sub>f</sub>H°(0 K) is identical to the one given above; it is different at all other temperatures. For example, Δ<sub>f</sub>H°(298.15 K) for pure triplet methylene is nominally lower by 0.005 kJ mol<sup>-1</sup> from the value given above (which is well outside the stated significant digits), but at 1000 K the difference in the enthalpies becomes 1.1 kJ mol<sup>-1</sup> and at 3000 K it becomes 6.8 kJ mol<sup>-1</sup>. Also, for pure triplet methylene:

C <sup>o</sup> <sub>p</sub> (298.15 K)=35.014 J K <sup>-1</sup> mol <sup>-1</sup>	H°(298.15 K)–H°(0 K)=10.027 kJ mol <sup>-1</sup>
S°(298.15 K)=194.418 J K <sup>-1</sup> mol <sup>-1</sup> .	

## Literature Data for the Enthalpy of Formation at 298.15 K

Δ <sub>f</sub> H°/kJ mol <sup>-1</sup>	Authors and Reference	Method <sup>a</sup>	Comments
<b>Measurements</b>			
387.4 <sup>b</sup> ±2.9	Chupka and Lifshitz (1967) <sup>1</sup>	PIMS-PIC	(1a)
<396 <sup>b</sup> ±2	Chupka (1968) <sup>2</sup>	PIMS-PIC	(1b)
391.3 <sup>b</sup> ±1.8	McCulloh and Dibeler (1976) <sup>3</sup>	PIMS-PIC	(1c)
388.6 <sup>b</sup> ±2.1 <sup>c</sup>	Lengel and Zare (1978) <sup>4</sup>	SPEC	(1d)
389.4 <sup>b</sup> ±2.1 <sup>c</sup>	Feldmann <i>et al.</i> (1978) <sup>5</sup>	SPEC	(1e)
394.4 <sup>b</sup> ±3.0 <sup>c</sup>	Hayden <i>et al.</i> (1982) <sup>6</sup>	SPEC	(1f)
392.4 <sup>b</sup> ±1.6 <sup>c</sup>	Chen <i>et al.</i> (1988) <sup>7</sup>	SPEC	(1g)
390.3±0.7	Litorja and Ruscic (1998) <sup>8</sup>	PIMS-PIC	(1h)
391.3 <sup>b</sup> ±0.7	Willitsch <i>et al.</i> (2002) <sup>9</sup>	PES-PIC	(1i)
<b>Computations</b>			
387.9±11.6 <sup>c</sup>	Melius (1990) <sup>10</sup>	BAC-MP4	(1j)
389.7 <sup>b</sup> ±2.5 <sup>c</sup>	Peterson and Dunning (1997) <sup>11</sup>	CCSD(T)	(1k)
389.2 <sup>b</sup> ±1.2 <sup>c</sup>	Doltsinis and Knowles (1997) <sup>12</sup>	MRCI	(1l)
396.2±13 <sup>c</sup>	Curtiss <i>et al.</i> (1998) <sup>13</sup>	CBS-Q	(1m)
386.6±7.9 <sup>c</sup>	Curtiss <i>et al.</i> (1998) <sup>14</sup>	G3	(1n)
391.0±1.9 <sup>c</sup>	Parthiban and Martin (2001) <sup>15</sup>	W2	(1o)
385.2±7.8 <sup>c</sup>	Janoschek and Rossi (2002) <sup>16</sup>	G3MP2B3	(1p)
390.87 <sup>b+0.68/-0.64</sup>	Császár <i>et al.</i> (2003) <sup>17</sup>	FPA	(1q)
<b>Reviews and Evaluations</b>			
390.4	NBS (1982) <sup>18</sup>	TT-U	(1r)
386.4±4.2	JANAF (1985) <sup>19</sup>	CDE	(1s)
390.4±4	Gurvich <i>et al.</i> (1991) <sup>20</sup>	CDE	(1t)
387.1 <sup>b</sup> ±2.9 <sup>c</sup>	Berkowitz <i>et al.</i> (1994) <sup>21</sup>	CDE	(1u)
390.4±4	NIST CCCBDB (1999) <sup>22</sup>	TT-A	(1v)
390.4±0.8	Ruscic <i>et al.</i> (1999) <sup>23</sup>	CDE-TN	(1w)
390.4	CRC HCP (2001) <sup>24</sup>	TT-U	(1x)
390.4±4	Kerr and Stocker (2001) <sup>25</sup>	TT-A	(1y)
390.4±4	Atkinson <i>et al.</i> (2000) <sup>26</sup>	TT-A	(1z)
390.4±4	Burcat (2001) <sup>27</sup>	TT-A	(1aa)
390.4±0.8	Sander <i>et al.</i> (2003) <sup>28</sup>	TT-A	(1bb)
386.4	NIST WebBook (2003) <sup>29</sup>	TT-A	(1cc)

<sup>a</sup>PIMS-PIC: positive ion cycle based on combining photoionization measurements of fragment appearance energy ( $E_{ap}$ ) from a stable molecule with ionization energy ( $E_i$ ) of the radical; SPEC: spectroscopy; PES-PIC: positive ion cycle based on combining the ionization energy, derived by using photoelectron spectroscopy, with the enthalpy of formation of the appropriate cation; CDE: critical data evaluation; CDE-TN: critical data evaluation through a thermochemical network; TT-U: unannotated tabulation of thermodynamic data; and TT-A: annotated tabulation of thermodynamic data.

<sup>b</sup>The quoted value was either not given explicitly by the author(s) or it was recalculated using auxiliary thermochemical values that differ from those used by the original authors; see individual comments for additional details.

<sup>c</sup>The uncertainty was either not given explicitly by the original author(s) or it has been modified; see individual comments for further explanations.

### Comments on the Enthalpies of Formation

(1a) Photoionization mass spectrometric study of methyl radical at several temperatures in the 810–1110 K range, producing the 0 K appearance energy of  $\text{CH}_2^+$  fragment of  $E_{\text{ap},0}(\text{CH}_2^+/\text{CH}_3) = 15.09 \pm 0.03$  eV. This value is combined with the adiabatic ionization energy of  $\text{CH}_2$  determined by Herzberg<sup>30–32</sup> (by extrapolating the  $nd\ ^3A_2$  Rydberg series from the first four members),  $E_{\text{i,ad}}(\text{CH}_2) = 10.396 \pm 0.003$  eV to produce  $D_0(\text{H}-\text{CH}_2) = 452.9 \pm 2.9$  kJ mol<sup>-1</sup>. However, the authors recognized that while the pyrolysis temperature itself was under experimental control, subsequent collisions relax the  $\text{CH}_3$  radical to an unknown temperature. Hence, the appearance energy was extracted by an unusual procedure: instead of the customary threshold extrapolation method, which entails accurate knowledge of the sample temperature, they made use of the inflection point at the foot of the fragment yield curve. While this approach is essentially correct, in practice it leads to considerable uncertainty. Their  $D_0(\text{H}-\text{CH}_2)$ , when combined with the CODATA<sup>33</sup> recommended values  $\Delta_f H^\circ_{298}(\text{H}) = 217.998 \pm 0.006$  kJ mol<sup>-1</sup>,  $[H^\circ(298.15\text{ K}) - H^\circ(0\text{ K})](\text{H}) = 6.197 \pm 0.001$  kJ mol<sup>-1</sup>, with  $[H^\circ(298.15\text{ K}) - H^\circ(0\text{ K})](\text{CH}_2) = 10.032$  kJ mol<sup>-1</sup> given below, and with  $\Delta_f H^\circ_{298}(\text{CH}_3) = 146.7 \pm 0.3$  kJ mol<sup>-1</sup> and  $[H^\circ(298.15\text{ K}) - H^\circ(0\text{ K})](\text{CH}_3) = 10.366$  kJ mol<sup>-1</sup> given elsewhere in this evaluation, yields the value listed in the table.

(1b) Photoionization mass spectrometric study of methane. An estimated upper limit, based on Herzberg's<sup>30–32</sup>  $E_{\text{i,ad}}(\text{CH}_2)$  and an upper limit to the fragment appearance energy of the  $\text{CH}_2^+$  fragment from  $\text{CH}_4$ ,  $E_{\text{ap},0}(\text{CH}_2^+/\text{CH}_4) < 15.19 \pm 0.02$  eV. The latter process, corresponding to  $\text{H}_2$  elimination that has to compete with a well-developed lower-energy process leading to  $\text{CH}_3^+$  fragment, is relatively weak and expected to suffer from a "kinetic shift." The value listed in the table is based on the resulting upper limit to the enthalpy for the  $\text{H}_2$  elimination from methane at 0 K of  $462.6 \pm 2.0$  kJ mol<sup>-1</sup> together with  $\Delta_f H^\circ_{298}(\text{CH}_4) = -74.60 \pm 0.30$  kJ mol<sup>-1</sup>,  $[H^\circ(298.15\text{ K}) - H^\circ(0\text{ K})](\text{CH}_4) = 10.016$  kJ mol<sup>-1</sup> from Gurvich *et al.*,<sup>20</sup>  $[H^\circ(298.15\text{ K}) - H^\circ(0\text{ K})](\text{H}_2) = 8.468 \pm 0.001$  kJ mol<sup>-1</sup> from CODATA,<sup>33</sup> and  $[H^\circ(298.15\text{ K}) - H^\circ(0\text{ K})](\text{CH}_2) = 10.032$  kJ mol<sup>-1</sup> given below.

(1c) Photoionization mass spectrometric study of methane and ketene. Based on the upper limit  $E_{\text{ap},0}(\text{CH}_2^+/\text{CH}_4) \leq 15.16 \pm 0.02$  eV and auxiliary thermochemical values given in (1b) above,  $\Delta_f H^\circ_{298}(\text{CH}_2) \leq 394 \pm 2$  kJ mol<sup>-1</sup>. From the study of ketene,  $E_{\text{ap},0}(\text{CH}_2^+/\text{CH}_2\text{CO}) = 13.729 \pm 0.008$  eV. When combined with Herzberg's<sup>30–32</sup>  $E_{\text{i,ad}}(\text{CH}_2)$ , this yields  $D_0(\text{CH}_2=\text{CO}) = 321.6 \pm 0.8$  kJ mol<sup>-1</sup>. This value, together with  $\Delta_f H^\circ_{298}(\text{CH}_2\text{CO}) = -47.7 \pm 1.6$  kJ mol<sup>-1</sup> from Nuttall *et al.*,<sup>34</sup>  $[H^\circ(298.15\text{ K}) - H^\circ(0\text{ K})](\text{CH}_2\text{CO}) = 11.796$  kJ mol<sup>-1</sup> estimated from known frequencies,<sup>35</sup>  $\Delta_f H^\circ_{298}(\text{CO}) = -110.53 \pm 0.17$  kJ mol<sup>-1</sup>, and  $[H^\circ(298.15\text{ K}) - H^\circ(0\text{ K})](\text{CO}) = 8.761 \pm 0.001$  kJ mol<sup>-1</sup> from CODATA,<sup>33</sup> and  $[H^\circ(298.15\text{ K}) - H^\circ(0\text{ K})](\text{CH}_2)$

$= 10.032$  kJ mol<sup>-1</sup> given below, yields the enthalpy of methylene listed in the table.

(1d) Photodissociation study of ketene on the singlet surface with laser induced fluorescence detection of  $\text{CH}_2$ , producing  $D_0(\text{CH}_2=\text{CO to } \tilde{a}^1A_1\text{CH}_2) = 356.5 \pm 1.3$  kJ mol<sup>-1</sup>. With the spectroscopic value of the separation between the singlet ( $\tilde{a}^1A_1$ ) and triplet ( $\tilde{X}^3B_1$ ) states of methylene<sup>36,37</sup> of  $3147 \pm 5$  cm<sup>-1</sup>, this leads to  $D_0(\text{CH}_2=\text{CO}) = 318.9 \pm 1.3$  kJ mol<sup>-1</sup> and hence the listed value for  $\Delta_f H^\circ_{298}(\text{CH}_2)$  [see (1c) above for auxiliary thermochemistry]. In the same study, the authors also report a singlet–triplet separation of  $2850 \pm 300$  cm<sup>-1</sup>, which implies slightly higher values  $D_0(\text{CH}_2=\text{CO}) = 322.4 \pm 3.8$  kJ mol<sup>-1</sup> and  $\Delta_f H^\circ_{298}(\text{CH}_2) = 392.1 \pm 4.1$  kJ mol<sup>-1</sup>.

(1e) Laser photodissociation study of ketene on the singlet surface with laser induced fluorescence detection of  $\text{CH}_2$ , producing  $D_0(\text{CH}_2=\text{CO to } \tilde{a}^1A_1\text{CH}_2) = 357.3 \pm 1.3$  kJ mol<sup>-1</sup>, and hence  $D_0(\text{CH}_2=\text{CO}) = 319.7 \pm 1.3$  kJ mol<sup>-1</sup> and the enthalpy of formation of methylene listed in the table [see (1c) above for auxiliary thermochemistry]. In the same study, the authors also report a singlet–triplet separation of  $3400 \pm 500$  cm<sup>-1</sup>, which would imply slightly lower values  $D_0(\text{CH}_2=\text{CO}) = 316.6 \pm 6.1$  kJ mol<sup>-1</sup> and  $\Delta_f H^\circ_{298}(\text{CH}_2) = 386.4 \pm 6.3$  kJ mol<sup>-1</sup>.

(1f) Laser photodissociation study of ketene with measurement of photofragment kinetic energies, producing  $D_0(\text{CH}_2=\text{CO}) = 324.7 (\pm 2.5)$  kJ mol<sup>-1</sup> and  $D_0(\text{CH}_2=\text{CO to } \tilde{a}^1A_1\text{CH}_2) = 360.2 \pm 2.1$  kJ mol<sup>-1</sup>. In the same study, the authors also report a singlet–triplet separation of  $3000 \pm 300$  cm<sup>-1</sup>. The value listed in the table follows directly from their  $D_0(\text{CH}_2=\text{CO})$  [see (1c) above for auxiliary thermochemistry]. Their  $D_0(\text{CH}_2=\text{CO to } \tilde{a}^1A_1\text{CH}_2)$  produces the slightly lower value of  $\Delta_f H^\circ_{298}(\text{CH}_2) = 392.3 \pm 2.7$  kJ mol<sup>-1</sup>. Finally, their  $D_0(\text{CH}_2=\text{CO to } \tilde{a}^1A_1\text{CH}_3)$ , coupled to their singlet–triplet separation, would produce  $D_0(\text{CH}_2=\text{CO}) = 324.3 \pm 4.2$  kJ mol<sup>-1</sup> and  $\Delta_f H^\circ_{298}(\text{CH}_2) = 394.1 \pm 4.5$  kJ mol<sup>-1</sup>, in good agreement with their direct measurement of the dissociation to triplet methylene.

(1g) Photodissociation study of ketene on the singlet surface with laser induced fluorescence detection of  $\text{CH}_2$ , producing  $D_0(\text{CH}_2=\text{CO to } \tilde{a}^1A_1\text{CH}_2) = 30116.2 \pm 0.4$  cm<sup>-1</sup>  $= 360.270 \pm 0.005$  kJ mol<sup>-1</sup> and, from the best available singlet–triplet separation,<sup>36,37</sup>  $D_0(\text{CH}_2=\text{CO}) = 26969 \pm 6$  cm<sup>-1</sup>  $= 322.62 \pm 0.06$  kJ mol<sup>-1</sup> and hence the listed enthalpy of formation of methylene [see (1c) above for auxiliary thermochemistry].

(1h) Combined photoionization mass spectrometric study of methyl and methylene radicals. From measurements of the  $\text{CH}_2^+$  fragmentation threshold from methyl that has been well equilibrated at 298 K, and careful fitting of the fragment yield, the study reports  $E_{\text{ap},0}(\text{CH}_2^+/\text{CH}_3) = 15.120 \pm 0.006$  eV. From measurements of parent ionization of methylene, the study finds  $E_{\text{i,ad}}(\text{CH}_2) = 10.393 \pm 0.011$  eV, in very good agreement with Herzberg's value of  $10.396 \pm 0.003$  eV. The two measured values produce  $D_0(\text{H}-\text{CH}_2) = 456.1 \pm 0.8$  kJ mol<sup>-1</sup>, and, with auxiliary

thermochemistry given in (1c) above,  $\Delta_f H^\circ_{298}(\text{CH}_2) = 390.6 \pm 1.3 \text{ kJ mol}^{-1}$ , while the combination of their appearance energy with Herzberg's<sup>30–32</sup>  $E_{i,\text{ad}}(\text{CH}_2) = 10.396 \pm 0.003 \text{ eV}$  produces  $D_0(\text{H}-\text{CH}_2) = 455.8 \pm 0.7 \text{ kJ mol}^{-1}$ . The latter bond dissociation energy is the basis for the listed enthalpy.

(1i) Photoelectron spectroscopic (ZEKE) study of  $\text{CH}_2$ , producing  $E_{i,\text{ad}}(\text{CH}_2) = 10.3864 \pm 0.0004 \text{ eV}$  ( $83\,772 \pm 3 \text{ cm}^{-1}$ ). With  $E_{\text{ap},0}(\text{CH}_2^+/\text{CH}_3) = 15.120 \pm 0.006 \text{ eV}$  from Litorja and Ruscic,<sup>8</sup> this results in  $D_0(\text{H}-\text{CH}_2) = 456.7 \pm 0.6 \text{ kJ mol}^{-1}$ , and, with auxiliary thermochemistry given in (1c) above, the enthalpy of formation of methylene listed in the table.

(1j) BAC-MP4 *ab initio* computations. The originally quoted uncertainty of  $\pm 5.8 \text{ kJ mol}^{-1}$  was multiplied by factor of 2 to bring it closer to the desired 95% confidence limit.

(1k) CCSD(T)/cc-pVnZ *ab initio* calculations extrapolated to complete basis set and corrected for core–valence effects produce  $D_0(\text{H}-\text{CH}_2) = 455.4 \text{ kJ mol}^{-1}$  after inclusion of ZPE. An estimated standard deviation of  $0.3 \text{ kcal mol}^{-1}$  has been quoted by the authors for the sequential set of bond dissociation energies of  $\text{CH}_4$ ; the uncertainty listed in the table corresponds to 2 s.d.

(1l) MRCI calculations using cc-pVnZ ( $n=2-6$ ) basis sets and CCSD(T)/cc-pCVnZ ( $n=2-5$ ) computations for core–valence correlation energies. The “best estimate” 0 K value for the enthalpy of formation of triplet methylene given by the authors is  $388.7 \pm 0.6 \text{ kJ mol}^{-1}$ . The originally quoted uncertainty has been multiplied by 2 to bring it closer to the desired 95% uncertainty limit.

(1m) CBS-Q calculation. The reported average absolute deviation of  $1.57 \text{ kcal mol}^{-1}$  was multiplied by 2 to bring it closer to the desired 95% confidence limit. The equivalent CBS-q and CBS-4 enthalpies of formation are  $397.5 \pm 18$  and  $391.6 \pm 26 \text{ kJ mol}^{-1}$ , where the uncertainties have been obtained in an analogous way.

(1n) G3 *ab initio* calculation. The uncertainty quoted in the table corresponds approximately to 95% confidence limits, based on twice the average absolute deviation of  $0.94 \text{ kcal mol}^{-1}$  for the enthalpies in the G2/97 test set, which roughly corresponds to one standard deviation. At the G3(MP2) level of theory<sup>38</sup>  $\Delta_f H^\circ_{298}(\text{CH}_2) = 386.2 \pm 9.9 \text{ kJ mol}^{-1}$ , where the quoted uncertainty has been derived in a similar fashion as for the G3 value. At the G2 level of theory<sup>39</sup>  $\Delta_f H^\circ_{298}(\text{CH}_2) = 396.2 \pm 13.1 \text{ kJ mol}^{-1}$ .

(1o) W2 *ab initio* calculation. The uncertainty quoted in the table corresponds approximately to 95% confidence limits based on twice the average absolute deviation for the W2 test set of  $0.23 \text{ kcal mol}^{-1}$ , which corresponds roughly to 1 s.d. At the W1 level of theory  $\Delta_f H^\circ_{298}(\text{CH}_2) = 390.4 \pm 3.1 \text{ kJ mol}^{-1}$ , where the uncertainty has been obtained in an analogous way.

(1p) G3(MP2)//B3LYP *ab initio* calculations for 32 selected free radicals. The uncertainty given in the table corresponds approximately to 95% confidence limits based on twice the quoted average absolute deviation of  $3.9 \text{ kJ mol}^{-1}$  for the calculated set of radicals. Note that the average absolute de-

viation which corresponds roughly to 1 s.d. for all enthalpies in the G2/97 test set using the same method is very slightly larger:<sup>40</sup>  $4.7 \text{ kJ mol}^{-1}$  [see also (1n) above].

(1q) High-quality *ab initio* study, including higher-order coupled cluster and full CI benchmarks with extended basis sets extrapolated to CBS limits and very high level corrections.

(1r) Critical data evaluation, but does not provide a pedigree of the selected value nor does it quote an error bar, although the value seems to be quite close to that adopted by Gurvich *et al.*<sup>18</sup> [see (1t) below].

(1s) Extensive compilation of thermodynamic data. The  $\text{CH}_2$  properties have been last revised in December 1972. The enthalpy of formation is based on the original value from the PIMS-PIC determination of Chupka and Lifshitz<sup>1</sup> [see (1a) above], although other electron impact and older photoionization measurements, as well as a mass spectrometric equilibrium study have been considered. These produced an upper and lower limit to the enthalpy of 400 and  $364 \text{ kJ mol}^{-1}$ . The  $\text{CH}_2$  properties have not been revised in the new edition.<sup>41</sup>

(1t) Extensive compilation of thermodynamic data. The selected value is based on the PIMS-PIC determination by McCulloh and Dibeler<sup>3</sup> [see (1c) above], as well as a mass spectrometric equilibrium study, the photoionization study of Chupka and Lifshitz,<sup>1</sup> and a study of photochemical decomposition of ketene. The value is unchanged from the previous (Russian) edition.<sup>42</sup>

(1u) Critical data evaluation of R–H bond dissociation energies based on three methods: kinetic determinations, positive ion cycle determinations from photoelectron/photoionization measurements, and negative ion cycle determinations from photoelectron measurements of negative ions combined with gas phase acidities. In their table of recommended values there is no entry for  $\text{CH}_2$ . However, in the table of photoionization results, they list  $D_0(\text{H}-\text{CH}_2) = 452.7 \pm 2.9 \text{ kJ mol}^{-1}$ , based on the study of Chupka and Lifshitz.<sup>1</sup>

(1v) The compilation lists theoretical results at various levels of theory, but also makes a reference to one experimental benchmark. The quoted experimental benchmark value is from Gurvich *et al.*<sup>20</sup> [see (1t) above].

(1w) A critical evaluation of enthalpies of formation based on a local thermochemical network consisting of five nodes ( $\text{CH}_3$ ,  $\text{CH}_3^+$ ,  $\text{CH}_2$ ,  $\text{CH}_2^+$ , and ketene) and 14 most accurate measurements available at that time (appearance energies, ionization energies, and one calorimetric determination), including measurements from Refs. 1, 3, and 7 [see (1a), (1c), and (1g) above]. The reported value was produced by a statistical analysis of data followed by a simultaneous solution of the adjusted network.

(1x) The tabulation gives a list of compilations as sources, but no specific references for individual species. However, the value appears to correspond to that adopted by NBS Tables<sup>18</sup> [see (1r) above] and Gurvich *et al.*<sup>20</sup> [see (1t) above].

(1y) The tabulation cites Gurvich *et al.*<sup>20</sup> as a source for the

enthalpy value used to calculate  $D_{298}(\text{H}-\text{CH}_2) = 462.0 \pm 4 \text{ kJ mol}^{-1}$ .

(1z) Critical evaluation of atmospherically relevant kinetic data. Their table of enthalpy data lists Kerr and Stocker<sup>25</sup> [see (1y) above] as their source of  $\Delta_f H^\circ_{298}(\text{CH}_2)$ .

(1aa) Thermochemical database for combustion. Burcat quotes Gurvich *et al.*<sup>20</sup> as a source of  $\Delta_f H^\circ_{298}(\text{CH}_2)$ .

(1bb) Critical evaluation of atmospherically relevant kinetic data. The quoted value is from Ruscic *et al.*<sup>23</sup> [see (1w) above].

(1cc) An unevaluated tabulation of available values, listing the thermochemistry of  $\text{CH}_2$  from the NIST-JANAF Tables<sup>41</sup> [see (1s) above].

### Preferred Value of the Enthalpy of Formation

$$\Delta_f H^\circ(298.15 \text{ K}) = 391.2 \pm 1.6 \text{ kJ mol}^{-1}$$

$$\Delta_f H^\circ(0 \text{ K}) = 390.7 \pm 1.6 \text{ kJ mol}^{-1}$$

The measurements can be partitioned into two groups: one group relates the enthalpy of formation of  $\text{CH}_2$  to methyl and hence to methane, the other group to ketene. In the group of measurements relating methylene to methyl, the most accurate are the photoionization measurements of Litorja and Ruscic<sup>8</sup> and the photoelectron study of Willitsch *et al.*<sup>9</sup> In the second group, the most accurate determination is that of Chen *et al.*<sup>7</sup> All three measurements agree within their uncertainties. In addition, the measurements of Litorja and Ruscic<sup>8</sup> and of Willitsch *et al.*<sup>9</sup> agree well with the coarser measurement of Chupka and Lifshitz<sup>1</sup> and the two existing upper limits.<sup>2,3</sup> Similarly, the C=C bond dissociation energy of ketene,  $D_0(\text{CH}_2=\text{CO}) = 322.62 \pm 0.06 \text{ kJ mol}^{-1}$ , obtained from photodissociation studies by Chen *et al.*,<sup>7</sup> agrees reasonably well with the significantly coarser weighted average of the other three similar measurements ( $320 \pm 5 \text{ kJ mol}^{-1}$ ) and with the photoionization measurement on ketene by McCulloh and Dibeler<sup>3</sup> ( $321.6 \pm 0.8 \text{ kJ mol}^{-1}$ ). The latter measurement was revisited by Ruscic *et al.*<sup>23</sup> who obtain  $D_0(\text{CH}_2=\text{CO}) = 322.9 \pm 0.6 \text{ kJ mol}^{-1}$ , in excellent agreement with the more precise determination of Chen *et al.*<sup>7</sup>

The derivation of the enthalpy of formation of methylene from the C=C bond dissociation energy in ketene involves  $\Delta_f H^\circ(\text{CH}_2\text{CO})$ , which is on somewhat less firm ground than either methyl or methane. For this group of measurements, the values listed in the table are derived by using  $\Delta_f H^\circ_{298}(\text{CH}_2\text{CO})$  from Nuttall *et al.*<sup>34</sup> With the enthalpy of formation of ketene  $\Delta_f H^\circ_{298}(\text{CH}_2\text{CO}) = -49.6 \pm 0.9 \text{ kJ mol}^{-1}$ , inferred by Ruscic *et al.*,<sup>23</sup> who used a local

thermochemical network to find simultaneous solution to enthalpies of  $\text{CH}_3$ ,  $\text{CH}_2$ , and ketene, the listed values would have been uniformly lower by  $1.9 \text{ kJ mol}^{-1}$ , perhaps bringing the two groups in even closer agreement. However, the analysis of Ruscic *et al.*<sup>23</sup> pre-dates the more recent measurement of  $E_{i,\text{ad}}(\text{CH}_2)$  by Willitsch *et al.*<sup>9</sup> The enthalpy of formation of methylene arising from the combination of  $E_{i,\text{ad}}(\text{CH}_2)$  by Willitsch *et al.*<sup>9</sup> with  $E_{\text{ap},0}(\text{CH}_2^+/\text{CH}_3) = 15.120 \pm 0.006 \text{ eV}$  from Litorja and Ruscic,<sup>8</sup> together with  $D_0(\text{CH}_2=\text{CO to } \tilde{a}^1A_1 \text{ CH}_2)$  of Chen *et al.*<sup>7</sup> and the best available triplet-singlet separation,<sup>36,37</sup> suggests  $\Delta_f H^\circ_{298}(\text{CH}_2\text{CO}) = -48.8 \pm 0.7 \text{ kJ mol}^{-1}$ , midway between the value of Nuttall *et al.*<sup>34</sup> and Ruscic *et al.*<sup>23</sup>

The weighted average of the results of Litorja and Ruscic,<sup>8</sup> Willitsch *et al.*,<sup>9</sup> and Chen *et al.*<sup>7</sup> produces  $\Delta_f H^\circ_{298}(\text{CH}_2) = 391.0 \pm 1.9 \text{ kJ mol}^{-1}$ . The weighted average of all experimental results listed in the table (excluding the upper limit of Chupka<sup>1</sup>) produces  $\Delta_f H^\circ_{298}(\text{CH}_2) = 391.2 \pm 1.6 \text{ kJ mol}^{-1}$ , which is the currently recommended preferred value. The very small discrepancies between the values from the first group and values from the second group add slightly to the overall uncertainty. The two most accurate theoretical calculations, that of Császár *et al.*<sup>17</sup> and that of Parthiban and Martin,<sup>15</sup> are in outstanding agreement with the recommended value.

The preferred value corresponds to the recommended value of the C-H bond dissociation energy of methyl,  $D_0(\text{CH}_3) = 456.67 \pm 1.67 \text{ kJ mol}^{-1}$  ( $462.53 \pm 1.67 \text{ kJ mol}^{-1}$  at 298.15 K), or the formal reaction enthalpy of  $\text{H}_2$  elimination from  $\text{CH}_4$  resulting in triplet methylene,  $\Delta_f H^\circ_0(\text{CH}_4 \rightarrow \text{H}_2 + \text{CH}_2, \text{ triplet}) = 457.32 \pm 1.67 \text{ kJ mol}^{-1}$  ( $465.80 \pm 1.67 \text{ kJ mol}^{-1}$  at 298.15 K), when used with the preferred value for the enthalpy of methyl given elsewhere in this evaluation,  $\Delta_f H^\circ_{298}(\text{CH}_3) = 146.66 \pm 0.28 \text{ kJ mol}^{-1}$ , and the corresponding enthalpy increment,  $[H^\circ(298.15 \text{ K}) - H^\circ(0 \text{ K})](\text{CH}_3) = 10.366 \text{ kJ mol}^{-1}$ , together with auxiliary thermodynamic values from Gurvich *et al.*<sup>20</sup>  $\Delta_f H^\circ_{298}(\text{CH}_4) = -74.60 \pm 0.30 \text{ kJ mol}^{-1}$ ,  $[H^\circ(298.15 \text{ K}) - H^\circ(0 \text{ K})](\text{CH}_4) = 10.016 \text{ kJ mol}^{-1}$ , the CODATA<sup>33</sup> recommended values  $\Delta_f H^\circ_{298}(\text{H}) = 217.998 \pm 0.006 \text{ kJ mol}^{-1}$ ,  $[H^\circ(298.15 \text{ K}) - H^\circ(0 \text{ K})](\text{H}) = 6.197 \pm 0.001 \text{ kJ mol}^{-1}$ ,  $[H^\circ(298.15 \text{ K}) - H^\circ(0 \text{ K})](\text{C, graphite}) = 1.050 \pm 0.020 \text{ kJ mol}^{-1}$ ,  $[H^\circ(298.15 \text{ K}) - H^\circ(0 \text{ K})](\text{C}) = 6.536 \pm 0.001 \text{ kJ mol}^{-1}$ , and  $[H^\circ(298.15 \text{ K}) - H^\circ(0 \text{ K})](\text{H}_2) = 8.468 \pm 0.001 \text{ kJ mol}^{-1}$ , and the enthalpy increment for  $\text{CH}_2$  listed below,  $[H^\circ(298.15 \text{ K}) - H^\circ(0 \text{ K})](\text{CH}_2) = 10.032 \text{ kJ mol}^{-1}$ .



Geometry (distance in Å, angles in degrees)<sup>(2a)</sup>

Z matrix				Cartesian coordinates			
				x	y	z	
C				C	0.000 000	0.000 000	0.143 379
H	1	1.075		H	0.000 000	0.402 093	-0.853 590
H	1	1.075	2 133.93	H	0.000 000	-0.402 093	-0.853 590

Moments of inertia ( $10^{-47}$  kg m<sup>2</sup>)<sup>(2b)</sup>

$I_A = 0.379 \times 10^{-47}$  kg m<sup>2</sup>       $I_B = 3.313 \times 10^{-47}$  kg m<sup>2</sup>       $I_C = 3.897 \times 10^{-47}$  kg m<sup>2</sup>

Vibrational wave numbers in the electronic ground state  $\nu_i$ (cm<sup>-1</sup>)<sup>(2c)</sup>

3031 ( $a_1$ )      963.1 ( $a_1$ )      3190 ( $b_2$ )

Heat Capacity  $C_p^\circ$ , Entropy  $S^\circ$ , and Enthalpy Increment [ $H^\circ(T) - H^\circ(0\text{ K})$ ]<sup>(2d),(2e)</sup>  
 CH<sub>2</sub>( $\tilde{X}^3B_1$ ) (including both triplet and singlet excited states)

T/K	$C_p^\circ(T)$ (JK <sup>-1</sup> mol <sup>-1</sup> )	$S^\circ(T)$ (JK <sup>-1</sup> mol <sup>-1</sup> )	$[H^\circ(T) - H^\circ(0\text{ K})]$ (kJ mol <sup>-1</sup> )
150	33.327	171.125	4.990
200	33.657	180.750	6.663
250	34.305	188.325	8.361
298.15	35.130	194.436	10.032
300	35.164	194.653	10.097
350	36.107	200.144	11.879
400	37.061	205.028	13.708
500	38.902	213.497	17.507
600	40.667	220.747	21.486
800	44.088	232.918	29.964
1000	47.209	243.100	39.101
1200	49.802	251.945	48.812
1500	52.639	263.384	64.207
2000	55.318	278.942	91.278
2500	56.609	291.441	119.298
3000	57.266	301.827	147.784

## 7-Constant NASA Polynomial

METHYLENE      JUN03 C 1.H 2. 0. 0.G 200.000 6000.000 14.02658 1  
 0.31104951E+01 0.37377952E-02 -0.13737198E-05 0.22305484E-09 -0.13356718E-13 2  
 0.45971595E+05 0.46279641E+01 0.38426183E+01 -0.73667687E-05 0.61697069E-05 3  
 -0.69668996E-08 0.26462098E-11 0.45863153E+05 0.12758447E+01 0.47050492E+05 4

## 9-Constant NASA Polynomial

METHYLENE      IUPAC Task Group on Selected Radicals  
 3 JUN03 C 1.00H 2.00 0.00 0.00 0.00 0 14.02658 391200.000  
 50.000 200.0007 -2.0 -1.0 0.0 1.0 2.0 3.0 4.0 0.0 10032.012  
 -0.420671934D+02 0.391404174D+01 0.386151561D+01 0.236445124D-02 -0.199247644D-04  
 0.715660664D-07 -0.495452802D-10 0.000000000D+00 0.458324663D+05 0.105346421D+01  
 200.000 1000.0007 -2.0 -1.0 0.0 1.0 2.0 3.0 4.0 0.0 10032.012  
 -0.221205597D+04 0.197311556D+03 0.170034375D+01 0.912972583D-02 -0.120887161D-04  
 0.100639092D-07 -0.332377013D-11 0.000000000D+00 0.450946103D+05 0.120796426D+02  
 1000.000 6000.0007 -2.0 -1.0 0.0 1.0 2.0 3.0 4.0 0.0 10032.012  
 0.203144487D+07 -0.710125987D+04 0.123667424D+02 -0.197780968D-02 0.397363730D-06  
 -0.416746166D-10 0.178524605D-14 0.000000000D+00 0.901316400D+05 -0.604813369D+02

CH<sub>2</sub>( $\tilde{X}^3B_1$ ) (triplet only, excluding singlet excited states)

T/K	$C_p^\circ(T)$ (JK <sup>-1</sup> mol <sup>-1</sup> )	$S^\circ(T)$ (JK <sup>-1</sup> mol <sup>-1</sup> )	$[H^\circ(T) - H^\circ(0\text{ K})]$ (kJ mol <sup>-1</sup> )
150	33.327	171.125	4.990
200	33.650	180.750	6.663
250	34.266	188.320	8.360
298.15	35.014	194.418	10.027
300	35.044	194.635	10.092
350	35.850	200.098	11.865
400	36.615	204.935	13.676
500	37.981	213.256	17.408
600	39.225	220.292	21.269
800	41.729	231.916	29.362
1000	44.247	241.500	37.962
1200	46.540	249.775	47.046
1500	49.319	260.474	61.445
2000	52.381	275.121	86.939
2500	54.180	287.020	113.617
3000	55.285	297.003	141.005

## 7-Constant NASA Polynomial

```

TRIPLET CH2      JUN03 C  1.H  2.  0.  0.G  200.000  6000.000  14.02658  1
0.31463189E+01  0.30367126E-02-0.99647444E-06  0.15048358E-09-0.85733552E-14  2
0.46041260E+05  0.47234171E+01  0.37175785E+01  0.12739126E-02  0.21734725E-05  3
-0.34885850E-08  0.16520887E-11  0.45872387E+05  0.17529794E+01  0.47050492E+05  4

```

## 9-Constant NASA Polynomial

```

TRIPLET CH2      IUPAC Task Group on Selected Radicals
3 JUN03 C  1.00H  2.00  0.00  0.00  0.00  0  14.02658  391200.000
50.000  200.0007 -2.0 -1.0  0.0  1.0  2.0  3.0  4.0  0.0  10027.357
0.215432176D+02-0.351004141D+00  0.397522197D+01  0.824472628D-03-0.876502765D-05
0.306600661D-07  0.945515135D-11  0.00000000D+00  0.458468204D+05  0.600717700D+00
200.000  1000.0007 -2.0 -1.0  0.0  1.0  2.0  3.0  4.0  0.0  10027.357
0.551715226D+04  0.105578694D+03  0.196850270D+01  0.967464448D-02-0.155434393D-04
0.135338510D-07-0.442461920D-11  0.00000000D+00  0.455632043D+05  0.102480525D+02
1000.000  6000.0007 -2.0 -1.0  0.0  1.0  2.0  3.0  4.0  0.0  10027.357
0.168256006D+07-0.530429713D+04  0.949126923D+01-0.629021046D-03  0.847808177D-07
-0.535674973D-11  0.100346421D-15  0.00000000D+00  0.795298631D+05-0.403922872D+02

```

## Comments on Molecular Data, Heat Capacity, Entropy, and Enthalpy Increment

(2a) The geometry reflects  $r_e(\text{CH}) = 1.075 \text{ \AA}$ , and  $\angle_e(\text{HCH}) = 133.93^\circ$ , from a theoretical analysis<sup>36(c),43</sup> of spectroscopic data obtained by laser magnetic resonance spectroscopy on various isotopomers of CH<sub>2</sub>.

(2b) The listed moments of inertia are based on the experimental rotational constants,<sup>37</sup>  $A_0 = 73.811 \text{ cm}^{-1}$ ,  $B_0 = 8.450 \text{ cm}^{-1}$ , and  $C_0 = 7.184 \text{ cm}^{-1}$ .

(2c) The symmetric stretch is apparently not known experimentally, and the corresponding value (in italics) has been obtained from a fully optimized B3LYP/6-31G(d) calculation.<sup>16</sup> The listed frequency was scaled by 0.9614.<sup>44</sup> The other two listed vibrational frequencies are experimentally determined fundamentals.<sup>37</sup>

(2d) The heat capacity, entropy, and enthalpy increment values were calculated in the rigid rotor-harmonic oscillator approximation using the molecular constants given above and

in the accompanying singlet CH<sub>2</sub> data sheet. The first table of thermochemical functions includes the following excited states<sup>36,37</sup> of methylene:  $T_0(\tilde{a}^1A_1) = 3147 \pm 5 \text{ cm}^{-1}$ , and  $T_0(\tilde{b}^1B_1) = 11497 \pm 10 \text{ cm}^{-1}$ . The values listed here differ significantly from those found in Gurvich *et al.*<sup>20</sup> and in the JANAF tables,<sup>19</sup> which were calculated within the same approximation, but using older values for the molecular constants. The second table provides the thermochemical functions of CH<sub>2</sub> as if the singlet states did not exist, and is useful in situations where triplet methylene is not equilibrated with singlet methylene.

(2e) The standard heat capacity, entropy, and enthalpy increment values reported in the NBS Tables<sup>18</sup> are  $C_p^\circ(298.15 \text{ K}) = 33.76 \text{ J mol}^{-1} \text{ K}^{-1}$ ,  $S^\circ(298.15 \text{ K}) = 194.87 \text{ J mol}^{-1} \text{ K}^{-1}$ ,  $H^\circ(298.15 \text{ K}) - H^\circ(0 \text{ K}) = 9.937 \text{ kJ mol}^{-1}$ , in the JANAF<sup>19</sup> and NIST-JANAF<sup>41</sup> thermochemical tables are  $C_p^\circ(298.15 \text{ K}) = 34.600 \text{ J mol}^{-1} \text{ K}^{-1}$ ,  $S^\circ(298.15 \text{ K}) = 193.931 \text{ J mol}^{-1} \text{ K}^{-1}$ ,

$H^\circ(298.15\text{ K}) - H^\circ(0\text{ K}) = 9.994\text{ kJ mol}^{-1}$ , in the compilation by Gurvich *et al.*<sup>20</sup> are  $C_p^\circ(298.15\text{ K}) = 33.763\text{ J mol}^{-1}\text{ K}^{-1}$ ,  $S^\circ(298.15\text{ K}) = 194.896\text{ J mol}^{-1}\text{ K}^{-1}$ , and  $H^\circ(298.15\text{ K}) - H^\circ(0\text{ K}) = 9.939\text{ kJ mol}^{-1}$ , in the *Thermochemical Database for Combustion*<sup>27</sup> are  $C_p^\circ(298.15\text{ K}) = 33.763\text{ J mol}^{-1}\text{ K}^{-1}$ ,  $S^\circ(298.15\text{ K}) = 194.899\text{ J mol}^{-1}\text{ K}^{-1}$ , and those obtained from G3MP2B3 computations<sup>16</sup> are  $C_p^\circ(298.15\text{ K}) = 34.61\text{ J mol}^{-1}\text{ K}^{-1}$ ,  $S^\circ(298.15\text{ K}) = 195.48\text{ J mol}^{-1}\text{ K}^{-1}$ , and  $H^\circ(298.15\text{ K}) - H^\circ(0\text{ K}) = 9.99\text{ kJ mol}^{-1}$ .

## References

- 1 W. A. Chupka and C. Lifshitz, *J. Chem. Phys.* **48**, 1109 (1968).
- 2 W. A. Chupka, *J. Chem. Phys.* **48**, 2337 (1968).
- 3 K. E. McCulloh and V. H. Dibeler, *J. Chem. Phys.* **64**, 4445 (1976).
- 4 R. K. Lengel and R. N. Zare, *J. Am. Chem. Soc.* **100**, 7495 (1978).
- 5 D. Feldmann, K. Meier, H. Zacharias, and K. H. Welge, *Chem. Phys. Lett.* **59**, 171 (1978).
- 6 C. C. Hayden, D. M. Neumark, K. Shobatake, R. K. Sparks, and Y. T. Lee, *J. Chem. Phys.* **76**, 3607 (1982).
- 7 I.-C. Chen, W. H. Green, Jr., and C. B. Moore, *J. Chem. Phys.* **89**, 314 (1988).
- 8 M. Litorja and B. Ruscic, *J. Chem. Phys.* **108**, 6748 (1998).
- 9 S. Willitsch, L. L. Imbach, and F. Merkt, *J. Chem. Phys.* **117**, 1939 (2002).
- 10 C. F. Melius, *Thermochemical Modeling: I. Application to Decomposition of Energetic Materials*, in *Chemistry and Physics of Energetic Materials*, edited by S. N. Bulusu (Kluwer, Dordrecht, 1990); see also (<http://z.ca.sandia.gov/~melius/>)
- 11 K. A. Peterson and T. H. Dunning, Jr., *J. Chem. Phys.* **106**, 4119 (1997).
- 12 N. L. Doltsinis and P. J. Knowles, *J. Chem. Soc. Faraday Trans.* **93**, 2025 (1997).
- 13 L. A. Curtiss, K. Raghavachari, P. C. Redfern, and B. B. Stefanov, *J. Chem. Phys.* **108**, 692 (1998).
- 14 L. A. Curtiss, K. Raghavachari, P. C. Redfern, V. Rassolov, and J. A. Pople, *J. Chem. Phys.* **109**, 7764 (1998).
- 15 S. Parthiban and J. M. L. Martin, *J. Chem. Phys.* **114**, 6014 (2001).
- 16 R. Janoschek and M. J. Rossi, *Int. J. Chem. Kinet.* **34**, 550 (2002).
- 17 A. G. Császár, M. L. Leininger, and V. Szalay, *J. Chem. Phys.* **118**, 10631 (2003).
- 18 D. D. Wagman, W. E. Evans, V. B. Parker, R. H. Schumm, I. Halow, S. M. Bailey, K. L. Churney, and R. L. Nuttall, *The NBS Tables of Chemical Thermodynamic Properties*, *J. Phys. Chem. Ref. Data* **11**, Suppl. 2 (1982).
- 19 M. W. Chase, Jr., C. A. Davies, J. R. Downey, Jr., D. J. Frurip, R. A. McDonald, and A. N. Syverud, *JANAF Thermochemical Tables*, 3rd ed., *J. Phys. Chem. Ref. Data* **14**, Suppl. 1 (1985).
- 20 L. V. Gurvich, I. V. Veys, and C. B. Alcock, *Thermodynamic Properties of Individual Substances*, 4th ed. (Hemisphere, New York, 1991), Vol. 2.
- 21 J. Berkowitz, G. B. Ellison, and D. Gutman, *J. Phys. Chem.* **98**, 2744 (1994).
- 22 Computational Chemistry Comparison and Benchmark DataBase (CCCBBDB), NIST 1999, see (<http://srdata.nist.gov/cccbdb/>)
- 23 B. Ruscic, M. Litorja, and R. L. Asher, *J. Phys. Chem. A* **103**, 8625 (1999); see also *ibid.* **104**, 8600E (2000).
- 24 *Standard Thermodynamic Properties of Chemical Substances*, in *CRC Handbook of Chemistry and Physics*, edited by D. Lide, 82nd ed. (CRC, Boca Raton, FL, 2001–2002).
- 25 J. A. Kerr and D. W. Stocker, *Strengths of Chemical Bonds*, in *CRC Handbook of Chemistry and Physics*, edited by D. Lide, 82nd ed. (CRC, Boca Raton, FL, 2001–2002).
- 26 R. Atkinson, D. L. Baulch, R. A. Cox, R. F. Hampson, Jr., J. A. Kerr, M. J. Rossi, and J. Troe, *J. Phys. Chem. Ref. Data* **29**, 167 (2000).
- 27 A. Burcat, TAE Report No. 867, Technion, Haifa, 2001 (see also (<ftp://ftp.technion.ac.il/pub/supported/aetdd/thermodynamics>)).
- 28 S. P. Sander, R. R. Friedl, D. M. Golden, M. J. Kurylo, R. E. Huie, V. L. Orkin, G. K. Moortgat, A. R. Ravishankara, C. E. Kolb, M. J. Molina, and B. J. Finlayson-Pitts, JPL Publication 02–25, NASA and JPL, February 1, 2003.
- 29 H. Y. Afeefy, J. F. Liebman, and S. E. Stein, *Neutral Thermochemical Data*, in *NIST Chemistry WebBook*, NIST Standard Reference Database Number 69, edited by P. J. Linstrom and W. G. Mallard (NIST, Gaithersburg, MD, 2003) (<http://webbook.nist.gov/>)
- 30 G. Herzberg, *Proc. R. Soc. London Ser. A* **262**, 291 (1961); see also G. Herzberg and J. Shoosmith, *Nature (London)* **183**, 1801 (1959).
- 31 G. Herzberg, *Can. J. Phys.* **39**, 1511 (1961).
- 32 G. Herzberg and J. W. C. Johns, *J. Chem. Phys.* **54**, 2276 (1971).
- 33 J. D. Cox, D. D. Wagman, and V. A. Medvedev, *CODATA Key Values for Thermodynamics* (Hemisphere, New York, 1989) (see also <http://www.codata.org/codata/databases/key1.html>)
- 34 R. L. Nuttall, A. H. Laufer, and M. V. Kilday, *J. Chem. Thermodyn.* **3**, 167 (1971).
- 35 For the enthalpy increment for ketene RRHO approximation is used, together with vibrational frequencies from: (a) C. B. Moore and G. Pimentel, *J. Chem. Phys.* **38**, 2816 (1963); (b) J. L. Duncan, A. M. Ferguson, J. Harpper, and K. H. Tonge, *J. Mol. Spectrosc.* **122**, 72 (1987); (c) J. L. Duncan, A. M. Ferguson, J. Harpper, and K. H. Tonge, *ibid.* **125**, 196 (1987).
- 36 (a) P. R. Bunker, P. Jensen, W. P. Kraemer, and R. Beardsworth, *J. Chem. Phys.* **85**, 3724 (1986); (b) P. R. Bunker and T. J. Sears, *ibid.* **83**, 4866 (1985); (c) P. Jensen and P. R. Bunker, *ibid.* **89**, 1327 (1988); (d) A. R. W. McKellar, P. R. Bunker, T. J. Sears, K. M. Evenson, R. J. Saykally, and S. R. Langhoff, *ibid.* **79**, 5251 (1983); (e) D. G. Leopold, K. K. Murray, A. E. Stevens Miller, and W. C. Lineberger, *ibid.* **83**, 4849 (1985).
- 37 M. E. Jacox, *J. Phys. Chem. Ref. Data* **32**, 1 (2003).
- 38 L. A. Curtiss, P. C. Redfern, K. Raghavachari, V. Rassolov, and J. A. Pople, *J. Chem. Phys.* **110**, 4703 (1999).
- 39 L. A. Curtiss, K. Raghavachari, G. W. Trucks, and J. A. Pople, *J. Chem. Phys.* **94**, 7221 (1991).
- 40 A. G. Baboul, L. A. Curtiss, P. C. Redfern, and K. Raghavachari, *J. Chem. Phys.* **110**, 7650 (1999).
- 41 M. W. Chase, Jr., *NIST-JANAF Thermochemical Tables*, 4th ed., *J. Phys. Chem. Ref. Data Monogr.* 9 (1998).
- 42 V. P. Glushko, L. V. Gurvich, G. A. Bergman, I. V. Veits, V. A. Medvedev, G. A. Khackhuruzov, and V. S. Yungman, *Termodinamicheski Svoistva Individual'nikh Veschestv*, 3rd ed. (Nauka, Moscow, 1979).
- 43 P. R. Bunker, *Kém. Közl.* **62**, 85 (1984).
- 44 A. P. Scott and L. Radom, *J. Phys. Chem.* **100**, 16502 (1996).

7.1.3. CH<sub>2</sub> Singlet Radical

## 7.1.3. Methylene Radical (singlet)

2465-56-7

CH <sub>2</sub> ( <sup>1</sup> A <sub>1</sub> )	C <sub>2v</sub> (σ <sub>ext</sub> =2)
Δ <sub>f</sub> H°(298.15 K) = 428.8 ± 1.6 kJ mol <sup>-1</sup>	Δ <sub>f</sub> H°(0 K) = 428.3 ± 1.6 kJ mol <sup>-1</sup>
C° <sub>p</sub> (298.15 K) = 33.781 J K <sup>-1</sup> mol <sup>-1</sup>	H°(298.15 K) - H°(0 K) = 9.940 kJ mol <sup>-1</sup>
S°(298.15 K) = 189.220 J K <sup>-1</sup> mol <sup>-1</sup>	p° = 100 000 Pa (1 bar)

## Literature Data for the Enthalpy of Formation at 298.15 K

Δ <sub>f</sub> H°/kJ mol <sup>-1</sup>	Authors and Reference	Method <sup>a</sup>	Comments
<b>Measurements</b>			
426.2 <sup>b</sup> ± 2.1 <sup>c</sup>	Lengel and Zare (1978) <sup>1</sup>	SPEC	(1a)
427.0 <sup>b</sup> ± 2.1 <sup>c</sup>	Feldmann <i>et al.</i> (1978) <sup>2</sup>	SPEC	(1b)
429.9 <sup>b</sup> ± 2.7 <sup>c</sup>	Hayden <i>et al.</i> (1982) <sup>3</sup>	SPEC	(1c)
429.9 <sup>b</sup> ± 1.6 <sup>c</sup>	Chen <i>et al.</i> (1988) <sup>4</sup>	SPEC	(1d)
428.4 <sup>b</sup> ± 1.3 <sup>c</sup>	Litorja and Ruscic (1998) <sup>5</sup>	PIMS-PIC	(1e)
<b>Computations</b>			
429.8 ± 15.9	Zachariah <i>et al.</i> (1996) <sup>6</sup>	BAC-MP4	(1f)
426.8 <sup>b</sup> ± 1.2 <sup>c</sup>	Doltsinis and Knowles (1997) <sup>7</sup>	MRCI	(1g)
430.5 ± 13 <sup>c</sup>	Curtiss <i>et al.</i> (1998) <sup>8</sup>	CBS-Q	(1h)
425.9 ± 7.9 <sup>c</sup>	Curtiss <i>et al.</i> (1998) <sup>9</sup>	G3	(1i)
429.3 ± 1.9 <sup>c</sup>	Parthiban and Martin (2001) <sup>10</sup>	W2	(1j)
424.7 ± 7.8 <sup>c</sup>	Janoschek and Rossi (2002) <sup>11</sup>	G3MP2B3	(1k)
428.52 <sup>b+0.78/-0.65</sup>	Császár <i>et al.</i> (2003) <sup>12</sup>	FPA	(1l)
<b>Reviews and Evaluations</b>			
428.1 ± 0.9	Ruscic <i>et al.</i> (1999) <sup>13</sup>	CDE-TN	(1m)
428.3 ± 4	Kerr and Stocker (2001) <sup>14</sup>	TT-A	(1n)
428.3 ± 4	Atkinson <i>et al.</i> (2000) <sup>15</sup>	TT-A	(1o)
424.7 ± 4	Burcat (2001) <sup>16</sup>	TT-A	(1p)
428.0 ± 0.8	Sander <i>et al.</i> (2003) <sup>17</sup>	TT-A	(1q)

<sup>a</sup>PIMS-PIC: positive ion cycle based on combining photoionization measurements of fragment appearance energy ( $E_{ap}$ ) from a stable molecule with ionization energy ( $E_i$ ) of the radical; SPEC: spectroscopy; CDE-TN: critical data evaluation through a thermochemical network; and TT-A: annotated tabulation of thermodynamic data.

<sup>b</sup>The quoted value was either not given explicitly by the author(s) or it was recalculated using auxiliary thermochemical values that differ from those used by the original authors; see individual comments for additional details.

<sup>c</sup>The uncertainty was either not given explicitly by the original author(s) or it has been modified; see individual comments for further explanations.

## Comments on the Enthalpies of Formation

(1a) Photodissociation study of ketene on the singlet surface with laser induced fluorescence detection of CH<sub>2</sub>, producing  $D_0(\text{CH}_2=\text{CO to } \tilde{a}^1A_1 \text{ CH}_2) = 356.5 \pm 1.3 \text{ kJ mol}^{-1}$ . In the same study, the authors also report the separation between the singlet ( $\tilde{a}^1A_1$ ) and triplet ( $\tilde{X}^3B_1$ ) states of methylene of  $2850 \pm 300 \text{ cm}^{-1}$ , which is slightly lower but otherwise in agreement with the best consensus value<sup>18,19</sup> of  $3147 \pm 5 \text{ cm}^{-1}$ . Their  $D_0(\text{CH}_2=\text{CO to } \tilde{a}^1A_1 \text{ CH}_2)$ , together with  $\Delta_f H^\circ_{298}(\text{CH}_2\text{CO}) = -47.7 \pm 1.6 \text{ kJ mol}^{-1}$  from Nuttall *et al.*,<sup>20</sup>  $[H^\circ(298.15 \text{ K}) - H^\circ(0 \text{ K})](\text{CH}_2\text{CO}) = 11.796 \text{ kJ mol}^{-1}$  estimated from known frequencies,<sup>21</sup>  $\Delta_f H^\circ_{298}(\text{CO}) = -110.53 \pm 0.17 \text{ kJ mol}^{-1}$  and  $[H^\circ(298.15 \text{ K}) - H^\circ(0 \text{ K})](\text{CO}) = 8.761 \pm 0.001 \text{ kJ mol}^{-1}$  from CODATA,<sup>22</sup> and  $[H^\circ(298.15 \text{ K}) - H^\circ(0 \text{ K})](\text{CH}_2) = 9.940 \text{ kJ mol}^{-1}$  given below, yields the enthalpy of methylene listed in the table.

(1b) Laser photodissociation study of ketene on the singlet surface with laser induced fluorescence detection of CH<sub>2</sub>, producing  $D_0(\text{CH}_2=\text{CO to } \tilde{a}^1A_1 \text{ CH}_2) = 357.3 \pm 1.3 \text{ kJ mol}^{-1}$ . The study reports a singlet-triplet splitting of  $3400 \pm 500 \text{ cm}^{-1}$ , slightly higher, but still in agreement with the best consensus value.<sup>18,19</sup> The value listed in the table is obtained from their  $D_0(\text{CH}_2=\text{CO to } \tilde{a}^1A_1 \text{ CH}_2)$  and auxiliary thermochemical values given in (1a) above.

(1c) Laser photodissociation study of ketene with measurement of photofragment kinetic energy, producing  $D_0(\text{CH}_2=\text{CO to } \tilde{a}^1A_1 \text{ CH}_2) = 360.2 \pm 2.1 \text{ kJ mol}^{-1}$ , which is the basis for the listed value together with auxiliary thermochemical values given in (1a) above. The separation between the singlet ( $\tilde{a}^1A_1$ ) and triplet ( $\tilde{X}^3B_1$ ) states of methylene reported in the same study is  $3000 \pm 300 \text{ cm}^{-1}$ , in good agreement with the best consensus value.<sup>18,19</sup> The authors also explicitly report  $D_0(\text{CH}_2=\text{CO to } \tilde{X}^3B_2 \text{ CH}_2) = 324.7$

( $\pm 2.5$ ) kJ mol<sup>-1</sup>, which, when coupled to the best available value for the singlet–triplet splitting<sup>18,19</sup> produces  $D_0(\text{CH}_2 = \text{CO to } \tilde{a}^1A_1 \text{ CH}_2) = 362.4(\pm 2.5)$  kJ mol<sup>-1</sup>, and would correspond to  $\Delta_f H^\circ_{298}(\text{CH}_2, \text{singlet}) = 432.0 \pm 3.0$  kJ mol<sup>-1</sup>.

(1d) Photodissociation study of ketene on the singlet surface with laser induced fluorescence detection of CH<sub>2</sub>, producing  $D_0(\text{CH}_2 = \text{CO to } \tilde{a}^1A_1 \text{ CH}_2) = 30\,116.2 \pm 0.4$  cm<sup>-1</sup> = 360.270  $\pm$  0.005 kJ mol<sup>-1</sup>, resulting in the value given in the table [see (1a) above for auxiliary thermochemistry].

(1e) Photoionization mass spectrometric study of methyl and methylene radicals. From measurements of the CH<sub>2</sub><sup>+</sup> fragmentation threshold from methyl equilibrated at 298.15 K, and fitting of the fragment yield, the study reports  $E_{\text{ap},0}(\text{CH}_2^+/\text{CH}_3) = 15.120 \pm 0.006$  eV. From measurements of parent ionization of methylene, the study finds  $E_{\text{i,ad}}(\text{CH}_2) = 10.393 \pm 0.011$  eV, in very good agreement with Herzberg's<sup>23–25</sup> value of 10.396  $\pm$  0.003 eV. Their measured  $E_{\text{i,ad}}(\text{CH}_2, \text{triplet})$ , together with the known singlet–triplet separation in methylene<sup>18,19</sup> implies  $E_{\text{i,ad}}(\text{CH}_2, \text{singlet}) = 10.003 \pm 0.011$  eV. With  $E_{\text{ap},0}(\text{CH}_2^+/\text{CH}_3)$ , this produces  $D_0(\text{H–CH}_2 \text{ to } \tilde{a}^1A_1 \text{ CH}_2) = 493.7 \pm 1.2$  kJ mol<sup>-1</sup> and hence  $\Delta_f H^\circ_{298}(\text{CH}_2, \text{singlet}) = 428.2 \pm 1.3$  kJ mol<sup>-1</sup>, when used in conjunction with the CODATA<sup>22</sup> recommended values  $\Delta_f H^\circ_{298}(\text{H}) = 217.998 \pm 0.006$  kJ mol<sup>-1</sup>,  $[H^\circ(298.15 \text{ K}) - H^\circ(0 \text{ K})](\text{H}) = 6.197 \pm 0.001$  kJ mol<sup>-1</sup>, with  $[H^\circ(298.15 \text{ K}) - H^\circ(0 \text{ K})](\text{CH}_2) = 9.940$  kJ mol<sup>-1</sup> given below, and with  $\Delta_f H^\circ_{298}(\text{CH}_3) = 146.7 \pm 0.3$  kJ mol<sup>-1</sup> and  $[H^\circ(298.15 \text{ K}) - H^\circ(0 \text{ K})] \times (\text{CH}_3) = 10.366$  kJ mol<sup>-1</sup> given elsewhere in this evaluation. Using Herzberg's<sup>23–25</sup>  $E_{\text{i,ad}}(\text{CH}_2, \text{triplet})$  in a similar fashion produces  $E_{\text{i,ad}}(\text{CH}_2, \text{singlet}) = 10.006 \pm 0.003$  eV,  $D_0(\text{H–CH}_2 \text{ to } \tilde{a}^1A_1 \text{ CH}_2) = 493.4 \pm 0.7$  kJ mol<sup>-1</sup> and  $\Delta_f H^\circ_{298}(\text{CH}_2, \text{singlet}) = 427.9 \pm 0.7$  kJ mol<sup>-1</sup>. Finally, using the recent  $E_{\text{i,ad}}(\text{CH}_2, \text{triplet}) = 10.3864 \pm 0.0004$  eV (83 772  $\pm$  3 cm<sup>-1</sup>) of Willitsch *et al.*<sup>26</sup> leads to  $E_{\text{i,ad}}(\text{CH}_2, \text{singlet}) = 9.996 \pm 0.001$  eV,  $D_0(\text{H–CH}_2 \text{ to } \tilde{a}^1A_1 \text{ CH}_2) = 494.4 \pm 0.6$  kJ mol<sup>-1</sup> and  $\Delta_f H^\circ_{298}(\text{CH}_2, \text{singlet}) = 428.8 \pm 0.7$  kJ mol<sup>-1</sup>. The weighted average of these three approaches is  $\Delta_f H^\circ_{298}(\text{CH}_2, \text{singlet}) = 428.4 \pm 1.3$  kJ mol<sup>-1</sup>, which is the value given in the table.

(1f) BAC-MP4 *ab initio* computations. The originally quoted uncertainty,  $\pm 15.9$  kJ mol<sup>-1</sup>, is rather large, probably reflecting the fact that methylene is a classical example of a multi-reference system; it is unclear if its intended meaning is one standard deviation or 95% confidence limit.

(1g) MRCI calculations using cc-pVnZ ( $n = 2–6$ ) basis sets and CCSD(T)/cc-pCVnZ ( $n = 2–5$ ) computations for core–valence correlation energies. The “best estimate” 0 K value for the enthalpy of formation of singlet methylene given by the authors is 426.4  $\pm$  0.6 kJ mol<sup>-1</sup>. The originally quoted uncertainty has been multiplied by 2 to bring it closer to the desired 95% uncertainty limit.

(1h) CBS-Q calculation. The reported average absolute deviation of 1.57 kcal mol<sup>-1</sup> was multiplied by 2 to bring it closer to the desired 95% confidence limit. The equivalent CBS-q and CBS-4 enthalpies of formation are 427.6

$\pm 18^\circ$  kJ mol<sup>-1</sup> and 437.6  $\pm$  26 kJ mol<sup>-1</sup>, where the uncertainties have been obtained in an analogous way.

(1i) G3 *ab initio* calculation. The uncertainty quoted in the table corresponds approximately to 95% confidence limits, based on twice the average absolute deviation of 0.94 kcal mol<sup>-1</sup> for the enthalpies in the G2/97 test set, which roughly corresponds to 1 s.d. At the G3(MP2) level of theory<sup>27</sup>  $\Delta_f H^\circ_{298}(\text{CH}_2, \text{singlet}) = 425.5 \pm 9.9$  kJ mol<sup>-1</sup>, where the quoted uncertainty has been derived in a similar fashion as for the G3 value. At the G2 level of theory<sup>28</sup>  $\Delta_f H^\circ_{298}(\text{CH}_2, \text{singlet}) = 424.3 \pm 13.1$  kJ mol<sup>-1</sup>.

(1j) W2 *ab initio* calculation. The uncertainty quoted in the table corresponds approximately to 95% confidence limits based on twice the average absolute deviation for the W2 test set of 0.23 kcal mol<sup>-1</sup>, which corresponds roughly to 1 s.d. At the W1 level of theory  $\Delta_f H^\circ_{298}(\text{CH}_2, \text{singlet}) = 428.8 \pm 3.1$  kJ mol<sup>-1</sup>, where the uncertainty has been obtained in an analogous way.

(1k) G3(MP2)//B3LYP *ab initio* calculations for 32 selected free radicals. The uncertainty given in the table corresponds approximately to 95% confidence limits based on twice the quoted average absolute deviation of 3.9 kJ mol<sup>-1</sup> for the calculated set of radicals, which corresponds roughly to 1 s.d. Note that the average absolute deviation for all enthalpies in the G2/97 test set using the same method is very slightly larger:<sup>29</sup> 4.7 kJ mol<sup>-1</sup> [see also (1i) above].

(1l) High-quality *ab initio* study, including higher-order coupled cluster and full CI benchmarks with extended basis sets extrapolated to CBS limits and very high level corrections.

(1m) A critical evaluation of enthalpies of formation based on a local thermochemical network consisting of five nodes (CH<sub>3</sub>, CH<sub>3</sub><sup>+</sup>, CH<sub>2</sub>, CH<sub>2</sub><sup>+</sup>, and ketene) and 14 most accurate measurements available at the time (appearance energies, ionization energies, and one calorimetric determination). The reported value was produced by a statistical analysis of data followed by a simultaneous solution of the adjusted network.

(1n) The tabulation cites Gurvich *et al.*<sup>30</sup> combined with Bunker and Sears<sup>18(b)</sup> as a source for the enthalpy.

(1o) Critical evaluation of atmospherically relevant kinetic data. Their table of enthalpy data lists Kerr and Stocker<sup>14</sup> [see (1n) above] as their source of  $\Delta_f H^\circ_{298}(\text{CH}_2, \text{singlet})$ .

(1p) Thermochemical database for combustion. Burcat quotes Melius<sup>31</sup> BAC-MP4 as a source of  $\Delta_f H^\circ_{298}(\text{CH}_2, \text{singlet})$ .

(1q) Critical evaluation of atmospherically relevant kinetic data. The quoted value has been obtained by applying the triplet–singlet separation in methylene<sup>18,19</sup> of 3147  $\pm$  5 cm<sup>-1</sup> to the selected enthalpy of formation  $\Delta_f H^\circ_0(\text{CH}_2, \text{triplet}) = 390.4 \pm 0.8$  kJ mol<sup>-1</sup>, which has been adopted from Ruscic *et al.*<sup>13</sup>

### Preferred Value of the Enthalpy of Formation

$$\Delta_f H^\circ(298.15 \text{ K}) = 428.8 \pm 1.6 \text{ kJ mol}^{-1}$$

$$\Delta_f H^\circ(0 \text{ K}) = 428.3 \pm 1.6 \text{ kJ mol}^{-1}$$

The preferred value  $\Delta_f H^\circ_{298}(\text{CH}_2, \text{singlet}) = 428.8 \pm 1.6 \text{ kJ mol}^{-1}$  corresponds to the selected enthalpy of formation of triplet methylene  $\Delta_f H^\circ_0(\text{CH}_2, \text{triplet}) = 391.2 \pm 1.6 \text{ kJ mol}^{-1}$ , combined with the best available value for the separation between the singlet ( $\tilde{a}^1A_1$ ) and triplet ( $\tilde{X}^3B_1$ ) states of methylene<sup>18,19</sup> of  $3147 \pm 5 \text{ cm}^{-1}$ . The preferred value is in outstanding agreement with the weighted average of all listed experimental results,  $\Delta_f H^\circ_{298}(\text{CH}_2) = 428.3 \pm 1.9 \text{ kJ mol}^{-1}$ , and also with the two most accurate theoretical calculations, that of Császár *et al.*<sup>12</sup> and that of Parthiban and Martin.<sup>10</sup>

The preferred value corresponds to the recommended value of the C–H bond dissociation energy of methyl to singlet methylene  $D_0(\text{H}-\text{CH}_2 \text{ to } \tilde{a}^1A_1 \text{ CH}_2) = 494.31 \pm 1.67 \text{ kJ mol}^{-1}$  ( $500.08 \pm 1.67 \text{ kJ mol}^{-1}$  at 298.15 K), or the reaction enthalpy of  $\text{H}_2$  elimination from  $\text{CH}_4$  on the singlet surface,  $\Delta_f H^\circ_0(\text{CH}_4 \rightarrow \text{H}_2 + \text{CH}_2, \text{singlet}) = 494.96$

$\pm 1.67 \text{ kJ mol}^{-1}$  ( $503.35 \pm 1.67 \text{ kJ mol}^{-1}$  at 298.15 K), when used with the preferred value for the enthalpy of methyl,  $\Delta_f H^\circ_{298}(\text{CH}_3) = 146.66 \pm 0.28 \text{ kJ mol}^{-1}$ , and the corresponding enthalpy increment,  $[H^\circ(298.15 \text{ K}) - H^\circ(0 \text{ K})](\text{CH}_3) = 10.366 \text{ kJ mol}^{-1}$ , together with auxiliary thermodynamic values from Gurvich *et al.*,<sup>30</sup>  $\Delta_f H^\circ_{298}(\text{CH}_4) = -74.60 \pm 0.30 \text{ kJ mol}^{-1}$ ,  $[H^\circ(298.15 \text{ K}) - H^\circ(0 \text{ K})](\text{CH}_4) = 10.016 \text{ kJ mol}^{-1}$ , CODATA<sup>29</sup> recommended values  $\Delta_f H^\circ_{298}(\text{H}) = 217.998 \pm 0.006 \text{ kJ mol}^{-1}$ ,  $[H^\circ(298.15 \text{ K}) - H^\circ(0 \text{ K})](\text{H}) = 6.197 \pm 0.001 \text{ kJ mol}^{-1}$ ,  $[H^\circ(298.15 \text{ K}) - H^\circ(0 \text{ K})](\text{C, graphite}) = 1.050 \pm 0.020 \text{ kJ mol}^{-1}$ ,  $[H^\circ(298.15 \text{ K}) - H^\circ(0 \text{ K})](\text{C}) = 6.536 \pm 0.001 \text{ kJ mol}^{-1}$ , and  $[H^\circ(298.15 \text{ K}) - H^\circ(0 \text{ K})](\text{H}_2) = 8.468 \pm 0.001 \text{ kJ mol}^{-1}$ , and the enthalpy increment for singlet  $\text{CH}_2$  listed below,  $[H^\circ(298.15 \text{ K}) - H^\circ(0 \text{ K})](\text{CH}_2) = 9.940 \text{ kJ mol}^{-1}$ .

Geometry (distance in Å, angles in degrees)<sup>(2a)</sup>

Z matrix				Cartesian coordinates				
				x	y	z		
C			C	0.000 000	0.000 000	-0.158 272		
H	1	1.107	H	0.000 000	-0.119 555	0.942 253		
H	1	1.107	2	102.4	H	0.000 000	0.119 555	0.942 253

Moments of inertia in the lowest singlet electronic state<sup>(2b)</sup>

$$I_A = 1.391 \times 10^{-47} \text{ kg m}^2 \quad I_B = 2.498 \times 10^{-47} \text{ kg m}^2 \quad I_C = 3.960 \times 10^{-47} \text{ kg m}^2$$

Vibrational wave numbers in the lowest singlet electronic state  $\nu_i(\text{cm}^{-1})$ <sup>(2c)</sup>

$$2806.0(a_1) \quad 1352.6(a_1) \quad 2865.0(b_2)$$

Heat Capacity  $C^\circ_p$ , Entropy  $S^\circ$ , and Enthalpy Increment  $[H^\circ(T) - H^\circ(0 \text{ K})]$ <sup>(2d)</sup>

$\text{CH}_2(\tilde{a}^1A_1)$  (including only singlet states)

T/K	$C^\circ_p(T)$ ( $\text{JK}^{-1} \text{ mol}^{-1}$ )	$S^\circ(T)$ ( $\text{JK}^{-1} \text{ mol}^{-1}$ )	$[H^\circ(T) - H^\circ(0 \text{ K})]$ ( $\text{kJ mol}^{-1}$ )
150	33.261	166.281	4.989
200	33.305	175.854	6.653
250	33.468	183.300	8.321
298.15	33.781	189.220	9.940
300	33.796	189.429	10.002
350	34.274	194.673	11.703
400	34.864	199.287	13.431
500	36.253	207.211	16.985
600	37.814	213.957	20.688
800	41.122	225.287	28.581
1000	44.231	234.805	37.122
1200	46.872	243.110	46.241
1500	49.974	253.919	60.791
2000	53.658	268.833	86.755
2500	56.335	281.108	114.285
3000	58.339	291.566	142.979

## 7-Constant NASA Polynomial

SINGLET CH2	JUN03 C	1.H	2.	0.	0.G	200.000	6000.000	14.02658	1
0.31350169E+01	0.28959393E-02	-0.81666809E-06	0.11357270E-09	-0.63626284E-14					2
0.50504050E+05	0.40603062E+01	0.41933133E+01	-0.23310518E-02	0.81567645E-05					3
-0.66298598E-08	0.19323320E-11	0.50366225E+05	-0.74673431E+00	0.51572728E+05					4

## 9-Constant NASA Polynomial

SINGLET CH2	IUPAC Task Group on Selected Radicals									
3 JUN03 C	1.00H	2.00	0.00	0.00	0.00	0.00	0.00	0.00	14.02658	428800.000
50.000	200.0007	-2.0	-1.0	0.0	1.0	2.0	3.0	4.0	0.0	9939.626
0.428286569D+02	-0.312687389D+01	0.409278287D+01	-0.143967938D-02	0.124079048D-04						
-0.566492577D-07	0.107845083D-09	0.000000000D+00	0.503870852D+05	-0.401884480D+00						
200.000	1000.0007	-2.0	-1.0	0.0	1.0	2.0	3.0	4.0	0.0	9939.626
-0.171248260D+05	0.286746303D+03	0.233336488D+01	0.364329463D-02	-0.184550149D-05						
0.166775532D-08	-0.749403072D-12	0.000000000D+00	0.490372633D+05	0.931123971D+01						
1000.000	6000.0007	-2.0	-1.0	0.0	1.0	2.0	3.0	4.0	0.0	9939.626
0.194687527D+06	-0.177764018D+04	0.650212651D+01	0.359050391D-03	0.676094197D-07						
-0.289156372D-10	0.221373722D-14	0.000000000D+00	0.606188535D+05	-0.187386842D+02						

### Comments on Molecular Data, Heat Capacity, Entropy, and Enthalpy Increment

(2a) The geometry reflects  $r_e(\text{CH}) = 1.107 \text{ \AA}$ , and  $\angle_e(\text{HCH}) = 102.4^\circ$ , as obtained from spectroscopic data.<sup>32</sup>

(2b) The listed moments of inertia are based on the experimental rotational constants<sup>19</sup>  $A_0 = 20.118 \text{ cm}^{-1}$ ,  $B_0 = 11.205 \text{ cm}^{-1}$ , and  $C_0 = 7.069 \text{ cm}^{-1}$ .

(2c) The listed vibrational frequencies are experimentally determined fundamentals.<sup>19</sup>

(2d) The heat capacity, entropy, and enthalpy increment values were calculated in the rigid rotor-harmonic oscillator approximation using the molecular constants given above. The  $\bar{a}^1A_1$  state of methylene, normally<sup>18,19</sup> at  $T_0(\bar{a}^1A_1) = 3147 \pm 5 \text{ cm}^{-1}$ , becomes the ground state ( $T_0 = 0$ ) of singlet methylene. The next excited singlet state<sup>18,19</sup> at  $T_0(\bar{b}^1B_1) = 11497 \pm 10 \text{ cm}^{-1}$  has also been included with a term value of  $T_0 = 11497 - 3147 \text{ cm}^{-1} = 8350 \text{ cm}^{-1}$ .

(2e) JANAF<sup>33</sup> and Gurvich *et al.*<sup>30</sup> do not report on singlet  $\text{CH}_2$ . The standard heat capacity and entropy values reported in the *Thermochemical Database for Combustion*<sup>16</sup> are  $C_p^\circ(298.15 \text{ K}) = 33.775 \text{ J mol}^{-1} \text{ K}^{-1}$  and  $S^\circ(298.15 \text{ K}) = 188.716 \text{ J mol}^{-1} \text{ K}^{-1}$ , and those obtained from G3MP2B3 computations<sup>11</sup> are  $C_p^\circ(298.15 \text{ K}) = 33.75 \text{ J mol}^{-1} \text{ K}^{-1}$ ,  $S^\circ(298.15 \text{ K}) = 189.27 \text{ J mol}^{-1} \text{ K}^{-1}$ , and  $H^\circ(298.15 \text{ K}) - H^\circ(0 \text{ K}) = 9.94 \text{ kJ mol}^{-1}$ .

### References

- R. K. Lengel and R. N. Zare, *J. Am. Chem. Soc.* **100**, 7495 (1978).
- D. Feldmann, K. Meier, H. Zacharias, and K. H. Welge, *Chem. Phys. Lett.* **59**, 171 (1978).
- C. C. Hayden, D. M. Neumark, K. Shobatake, R. K. Sparks, and Y. T. Lee, *J. Chem. Phys.* **76**, 3607 (1982).
- I.-C. Chen, W. H. Green, Jr., and C. B. Moore, *J. Chem. Phys.* **89**, 314 (1988).
- M. Litorja and B. Ruscic, *J. Chem. Phys.* **108**, 6748 (1998).
- M. R. Zachariah, P. R. Westmoreland, D. R. Burgess, Jr., W. Tsang, and C. F. Melius, *J. Phys. Chem. A* **100**, 8737 (1996); see also D. R. F. Burgess, Jr., M. R. Zachariah, W. Tsang, and P. R. Westmoreland, *Prog. Energy Combust. Sci.* **21**, 453 (1995).

- N. L. Doltsinis and P. J. Knowles, *J. Chem. Soc. Faraday Trans.* **93**, 2025 (1997).
- L. A. Curtiss, K. Raghavachari, P. C. Redfern, and B. B. Stefanov, *J. Chem. Phys.* **108**, 692 (1998).
- L. A. Curtiss, K. Raghavachari, P. C. Redfern, V. Rassolov, and J. A. Pople, *J. Chem. Phys.* **109**, 7764 (1998).
- S. Parthiban and J. M. L. Martin, *J. Chem. Phys.* **114**, 6014 (2001).
- R. Janoschek and M. J. Rossi, *Int. J. Chem. Kinet.* **34**, 550 (2002).
- A. G. Császár, M. L. Leininger, and V. Szalay, *J. Chem. Phys.* (in press 2003).
- B. Ruscic, M. Litorja, and R. L. Asher, *J. Phys. Chem. A* **103**, 8625 (1999); see also *ibid.* **104**, 8600E (2000).
- J. A. Kerr and D. W. Stocker, *Strengths of Chemical Bonds*, in *CRC Handbook of Chemistry and Physics*, edited by D. Lide Ed., 82nd ed. (CRC, Boca Raton, FL, 2001–2002).
- R. Atkinson, D. L. Baulch, R. A. Cox, R. F. Hampson, Jr., J. A. Kerr, M. J. Rossi, and J. Troe, *J. Phys. Chem. Ref. Data* **29**, 167 (2000).
- A. Burcat, TAE Report No. 867, Technion, Haifa, 2001, see also <ftp://ftp.technion.ac.il/pub/supported/aetdd/thermodynamics>
- S. P. Sander, R. R. Friedl, D. M. Golden, M. J. Kurylo, R. E. Huie, V. L. Orkin, G. K. Moortgat, A. R. Ravishankara, C. E. Kolb, M. J. Molina, and B. J. Finlayson-Pitts, JPL Publication 02-25, NASA and JPL, February 1, 2003.
- (a) P. R. Bunker, P. Jensen, W. P. Kraemer, and R. Beardsworth, *J. Chem. Phys.* **85**, 3724 (1986); (b) P. R. Bunker and T. J. Sears, *ibid.* **83**, 4866 (1985); (c) P. Jensen and P. R. Bunker, *ibid.* **89**, 1327 (1988); (d) A. R. W. McKellar, P. R. Bunker, T. J. Sears, K. M. Evenson, R. J. Saykally, and S. R. Langhoff, *ibid.* **79**, 5251 (1983); (e) D. G. Leopold, K. K. Murray, A. E. Stevens Miller, and W. C. Lineberger, *ibid.* **83**, 4849 (1985).
- M. E. Jacox, *J. Phys. Chem. Ref. Data* **32**, 1 (2003).
- R. L. Nuttall, A. H. Laufer, and M. V. Kilday, *J. Chem. Thermodyn.* **3**, 167 (1971).
- For the enthalpy increment for ketene the RRHO approximation is used, together with vibrational frequencies from: (a) C. B. Moore and G. Pimentel, *J. Chem. Phys.* **38**, 2816 (1963); (b) J. L. Duncan, A. M. Ferguson, J. Harpper, and K. H. Tonge, *J. Mol. Spectrosc.* **122**, 72 (1987); (c) **125**, 196 (1987).
- J. D. Cox, D. D. Wagman, and V. A. Medvedev, *CODATA Key Values for Thermodynamics*; (Hemisphere, New York, 1989) (see also <http://www.codata.org/codata/databases/key1.html>)
- G. Herzberg, *Proc. R. Soc. London Ser. A* **262**, 291 (1961); see also G. Herzberg and J. Shoosmith, *Nature (London)* **183**, 1801 (1959).
- G. Herzberg, *Can. J. Phys.* **39**, 1511 (1961).
- G. Herzberg and J. W. C. Johns, *J. Chem. Phys.* **54**, 2276 (1971).

- <sup>26</sup>S. Willitsch, L. L. Imbach, and F. Merkt, *J. Chem. Phys.* **117**, 1939 (2002).
- <sup>27</sup>L. A. Curtiss, P. C. Redfern, K. Raghavachari, V. Rassolov, and J. A. Pople, *J. Chem. Phys.* **110**, 4703 (1999).
- <sup>28</sup>L. A. Curtiss, K. Raghavachari, G. W. Trucks, and J. A. Pople, *J. Chem. Phys.* **94**, 7221 (1991).
- <sup>29</sup>A. G. Baboul, L. A. Curtiss, P. C. Redfern, and K. Raghavachari, *J. Chem. Phys.* **110**, 7650 (1999).
- <sup>30</sup>L. V. Gurvich, I. V. Veyts, and C. B. Alcock, *Thermodynamic Properties of Individual Substances*, 4th ed. (Hemisphere, New York, 1991), Vol. 2.
- <sup>31</sup>C. Melius, Database of 3500 species calculated by the BAC/MP4 method at Sandia National Laboratories, 1993 (<http://z.ca.sandia.gov/~melius/>)
- <sup>32</sup>H. Petek, D. J. Nesbitt, P. R. Ogilby, C. B. Moore, and D. A. Ramsay, *J. Chem. Phys.* **91**, 6566 (1989).
- <sup>33</sup>M. W. Chase, Jr., C. A. Davies, J. R. Downey, Jr., D. J. Frurip, R. A. McDonald, and A. N. Syverud, *JANAF Thermochemical Tables*, 3rd ed., *J. Phys. Chem. Ref. Data* **14**, Suppl. 1 (1985).



7.1.4. CH<sub>3</sub> Radical

## 7.1.4. Methyl radical

2229-07-4

CH <sub>3</sub> ( <sup>2</sup> A <sub>2</sub> '')	D <sub>3h</sub> (σ <sub>ext</sub> =6)
Δ <sub>f</sub> H°(298.15 K)=146.7±0.3 kJ mol <sup>-1</sup>	Δ <sub>f</sub> H°(0 K)=150.0±0.3 kJ mol <sup>-1</sup>
C <sup>o</sup> <sub>p</sub> (298.15 K)=38.417 J K <sup>-1</sup> mol <sup>-1</sup>	H°(298.15 K)–H°(0 K)=10.366 kJ mol <sup>-1</sup>
S°(298.15 K)=194.008 J K <sup>-1</sup> mol <sup>-1</sup>	p° = 100 000 Pa (1 bar)

## Literature Data for the Enthalpy of Formation at 298.15 K

Δ <sub>f</sub> H°/kJ mol <sup>-1</sup>	Authors and Reference	Method <sup>a</sup>	Comments
<b>Measurements</b>			
146.4 <sup>b</sup> ±0.5	Chupka (1968) <sup>1</sup>	PIMS-PIC	(1a)
146.8 <sup>b</sup> ±0.4	McCulloh and Dibeler (1976) <sup>2</sup>	PIMS-PIC	(1b)
144.4 <sup>b</sup> ±2.2 <sup>c</sup>	Traeger and McLoughlin (1981) <sup>3</sup>	PIMS-PIC	(1c)
145.4±1.7	Russel <i>et al.</i> (1988) <sup>4</sup>	KE	(1d)
148±3	Russel <i>et al.</i> (1988) <sup>5</sup>	KE	(1e)
146±1	Seetula <i>et al.</i> (1990) <sup>6</sup>	KE	(1f)
147.7±2.5	Nicovich <i>et al.</i> (1997) <sup>7</sup>	KE	(1g)
146.6±0.4	Litorja and Ruscic (1997) <sup>8</sup>	PIMS-PIC	(1h)
146.7 <sup>b</sup> ±0.4 <sup>c</sup>	Weitzel <i>et al.</i> (2000) <sup>9</sup>	PIMS-PIC	(1i)
<b>Computations</b>			
146.0±10.2 <sup>c</sup>	Zachariah <i>et al.</i> (1996) <sup>10</sup>	BAC-MP4	(1j)
146.6 <sup>b</sup> ±2.5 <sup>c</sup>	Peterson and Dunning (1997) <sup>11</sup>	CCSD(T)	(1k)
147.7±13 <sup>c</sup>	Curtiss <i>et al.</i> (1998) <sup>12</sup>	CBS-Q	(1l)
142.2±7.9 <sup>c</sup>	Curtiss <i>et al.</i> (1998) <sup>13</sup>	G3	(1m)
145.6±1.9 <sup>c</sup>	Parthiban and Martin (2001) <sup>14</sup>	W2	(1n)
144.0±7.8 <sup>c</sup>	Janoschek and Rossi (2002) <sup>15</sup>	G3MP2B3	(1o)
<b>Reviews and Evaluations</b>			
145.69	NBS (1982) <sup>16</sup>	TT-U	(1p)
146.9±0.8	McMillen and Golden (1982) <sup>17</sup>	CDE	(1q)
145.7±0.8	JANAF (1985) <sup>18</sup>	CDE	(1r)
146.3±0.5	Gurvich <i>et al.</i> (1991) <sup>19</sup>	CDE	(1s)
146.4±0.4	Berkowitz <i>et al.</i> (1994) <sup>20</sup>	CDE	(1t)
147±1	Tsang (1996) <sup>21</sup>	CDE	(1u)
146.3±0.5	NIST CCCBDB (1999) <sup>22</sup>	TT-A	(1v)
146.66±0.28	Ruscic <i>et al.</i> (1999) <sup>23</sup>	CDE-TN	(1w)
145.7	CRC HCP (2001) <sup>24</sup>	TT-U	(1x)
146.4±0.4	Kerr and Stocker (2001) <sup>25</sup>	TT-A	(1y)
146.4±0.4	Atkinson <i>et al.</i> (2000) <sup>26</sup>	TT-A	(1z)
146.9±1	Burcat (2001) <sup>27</sup>	TT-A	(1aa)
146.65±0.29	Sander <i>et al.</i> (2003) <sup>28</sup>	TT-A	(1bb)
145.7	NIST WebBook (2003) <sup>29</sup>	TT-A	(1cc)

<sup>a</sup>PIMS-PIC: positive ion cycle based on combining photoionization measurements of fragment appearance energy ( $E_{ap}$ ) from a stable molecule with ionization energy ( $E_i$ ) of the radical; KE: kinetic equilibrium study; CDE: critical data evaluation; CDE-TN: critical data evaluation through a thermochemical network; TT-U: unannotated tabulation of thermodynamic data; and TT-A: annotated tabulation of thermodynamic data.

<sup>b</sup>The quoted value was either not given explicitly by the author(s) or it was recalculated using auxiliary thermochemical values that differ from those used by the original authors; see individual comments for additional details.

<sup>c</sup>The uncertainty was either not given explicitly by the original author(s) or it has been modified; see individual comments for further explanations.

**Comments on the Enthalpies of Formation**

(1a) Photoionization mass spectrometric study of methane producing the 0 K appearance energy of CH<sub>3</sub><sup>+</sup> fragment of  $E_{ap,0}(\text{CH}_3^+/\text{CH}_4) = 14.320 \pm 0.004$  eV. This value was originally combined by Chupka with the adiabatic ionization en-

ergy of CH<sub>3</sub> determined by Herzberg<sup>30</sup> as  $E_{i,ad}(\text{CH}_3)/hc = 79392 \pm 5$  cm<sup>-1</sup> to produce  $D_0(\text{H}-\text{CH}_3) = 431.9 \pm 0.4$  kJ mol<sup>-1</sup>, implying  $\Delta_f H^\circ_{298}(\text{CH}_3) = 145.9 \pm 0.5$  kJ mol<sup>-1</sup>. However, Litorja and Ruscic<sup>8</sup> [see (1h) below] have subsequently shown that Herzberg's  $E_{i,ad}(\text{CH}_3)$  is

slightly too high. With the ZEKE value<sup>31</sup> for the adiabatic ionization term value of  $\text{CH}_3$  of  $79\,349 \pm 3 \text{ cm}^{-1}$ , the appearance energy of  $\text{CH}_3^+/\text{CH}_4$  of Chupka produces  $D_0(\text{H}-\text{CH}_3) = 432.4 \pm 0.4 \text{ kJ mol}^{-1}$ , corresponding to  $\Delta_f H^\circ_{298}(\text{CH}_3) = 146.4 \pm 0.5 \text{ kJ mol}^{-1}$ .

(1b) Photoionization mass spectrometric study of methane producing the 0 K appearance energy of  $\text{CH}_3^+$  fragment  $E_{\text{ap},0}(\text{CH}_3^+/\text{CH}_4) = 14.324 \pm 0.003 \text{ eV}$ . This was originally combined by McCulloh and Dibeler with Herzberg's<sup>30</sup>  $E_{\text{i,ad}}(\text{CH}_3)$  to produce  $D_0(\text{H}-\text{CH}_3) = 432.3 \pm 0.3 \text{ kJ mol}^{-1}$  and hence  $\Delta_f H^\circ_{298}(\text{CH}_3) = 146.3 \pm 0.4 \text{ kJ mol}^{-1}$ . With ZEKE<sup>31</sup>  $E_{\text{i,ad}}(\text{CH}_3)$  [see (1a) above and (1h) below],  $D_0(\text{H}-\text{CH}_3) = 432.8 \pm 0.3 \text{ kJ mol}^{-1}$ , corresponding to  $\Delta_f H^\circ_{298}(\text{CH}_3) = 146.8 \pm 0.4 \text{ kJ mol}^{-1}$ .

(1c) Photoionization mass spectrometric study of  $\text{CH}_3\text{Br}$  and  $\text{CH}_3\text{I}$ . The reported appearance energies of the  $\text{CH}_3^+$  fragment at 298.15 K are  $E_{\text{ap},298}(\text{CH}_3^+/\text{CH}_3\text{Br}) = 12.77 \pm 0.01 \text{ eV}$  and  $E_{\text{ap},298}(\text{CH}_3^+/\text{CH}_3\text{I}) = 12.18 \pm 0.01 \text{ eV}$ . The approach of Traeger and McLoughlin applies all the necessary thermal transformations from 298.15 to 0 K in one step, without explicitly giving  $E_{\text{ap},0}$  values. The two determinations produce an average value  $\Delta_f H^\circ_{298}(\text{CH}_3^+) = 1093.3 \pm 1.7 \text{ kJ mol}^{-1}$  (stationary electron convention), which relies on  $\Delta_f H^\circ_{298}(\text{CH}_3\text{Br}) = -37.2 \pm 0.8 \text{ kJ mol}^{-1}$  and  $\Delta_f H^\circ_{298}(\text{CH}_3\text{I}) = 15.5 \pm 0.8 \text{ kJ mol}^{-1}$  from Pedley and Rylance.<sup>32</sup> ZEKE<sup>31</sup>  $E_{\text{i,ad}}(\text{CH}_3)$  [see (1a) above and (1h) below] and additional 298.15–0 K corrections lead to the listed value. Herzberg's<sup>30</sup>  $E_{\text{i,ad}}(\text{CH}_3)$ , as used by Traeger and McLoughlin, produces slightly lower values. However, a closer inspection of the fragment ion yields in question suggests that the linear extrapolation used by Traeger and McLoughlin ignores inward curvature of the thresholds, resulting in too low  $E_{\text{ap}}$  values and hence a too low  $\Delta_f H^\circ(\text{CH}_3)$ . Linear analysis of all experimental values, discussed in conjunction with the selection of the preferred value, indicates that a larger nominal uncertainty,  $\pm 2.2 \text{ kJ mol}^{-1}$ , is more appropriate than the uncertainty of  $\pm 1.7 \text{ kJ mol}^{-1}$  that was given originally by the authors.

(1d) Reaction  $\text{CH}_3 + \text{HCl} \rightarrow \text{CH}_4 + \text{Cl}$  studied in a tubular reactor coupled to a photoionization MS. In the temperature range of 296–495 K, the activation energy of  $E_{\text{a,f}} = -5.9 \pm 1.3 \text{ kJ mol}^{-1}$  was obtained for the forward reaction. Reported literature data at 298–504 K were used to derive the activation energy of  $E_{\text{a,r}} = 13.0 \pm 1.3 \text{ kJ mol}^{-1}$  for the reverse reaction. Thus, a second-law value of  $\Delta_f H^\circ_{298}(\text{CH}_3) = 145.2 \pm 2.5 \text{ kJ mol}^{-1}$  is derived. In addition a third-law value of  $\Delta_f H^\circ_{298} = 145.6 \pm 1.3 \text{ kJ mol}^{-1}$  is obtained from the reaction Gibbs energy derived from the kinetic data of the forward and reverse reactions and the reaction entropy<sup>19</sup> of  $\Delta_r S^\circ_{298} = -29.7 \pm 1.7 \text{ J K}^{-1} \text{ mol}^{-1}$ .

(1e) Reaction  $\text{CH}_3 + \text{HBr} \rightarrow \text{CH}_4 + \text{Br}$  studied in a tubular reactor coupled to a photoionization MS. In the temperature range of 296–532 K, an activation energy of  $E_{\text{a,f}} = 1.3 \pm 0.9 \text{ kJ mol}^{-1}$  was derived for the forward reaction. The activation energy for the reverse reaction of  $E_{\text{a,r}} = 73.9 \pm 2.5 \text{ kJ mol}^{-1}$  was obtained from literature data of direct measurements for the  $t\text{-C}_4\text{H}_9 + \text{HBr}$  reaction and relative

rate data for several  $\text{Br} + \text{hydrocarbon}$  reactions. Finally, the second-law derivation was used to obtain the enthalpy of formation for  $\text{CH}_3$ .

(1f) Reaction  $\text{CH}_3 + \text{HI} \rightarrow \text{CH}_4 + \text{I}$  studied in a tubular reactor coupled to a photoionization MS. In the temperature range of 292–648 K, the rate coefficient expression of  $k_f = (4.5 \pm 0.8) \times 10^{-12} \exp[(1.2 \pm 0.6) \text{ kJ mol}^{-1}/RT] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  was obtained for the forward reaction. Kinetic data for the reverse reaction were taken from the literature.<sup>33</sup> Thus, a second-law and [with  $S^\circ_{298}(\text{CH}_3) = 194 \pm 0.4 \text{ J K}^{-1} \text{ mol}^{-1}$ ] a third-law enthalpy of formation of  $\Delta_f H^\circ_{298} = 150$  and  $145 \text{ kJ mol}^{-1}$ , respectively, have been derived. The value given in the table corresponds to their preferred value.

(1g) Laser flash photolysis/resonance fluorescence (Br atom monitoring) study of reaction  $\text{CH}_3 + \text{HBr} \rightarrow \text{CH}_4 + \text{Br}$ . In the temperature range of 257–422 K, the rate coefficient expression of  $k_f = (1.4 \pm 0.1) \times 10^{-12} \exp[(1.9 \pm 0.2) \text{ kJ mol}^{-1}/RT] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  was obtained for the forward reaction. This is combined with the best available kinetic data<sup>34</sup> for the reverse reaction,  $k_r = (1.7 \pm 0.9) \times 10^{-10} \exp[(-73.9 \pm 1.8) \text{ kJ mol}^{-1}/RT] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (in the temperature range 298–621 K) to obtain the second-law value and (with the appropriate entropies<sup>27</sup>) the third-law heat of formation for  $\text{CH}_3$ . The arithmetic mean of these, given as  $35.3 \pm 0.6 \text{ kcal mol}^{-1}$ , is listed in the table.

(1h) Reexamination of the  $\text{CH}_3^+$  fragment appearance potential from  $\text{CH}_4$  by photoionization mass spectrometry. The value  $E_{\text{ap},0}(\text{CH}_3^+/\text{CH}_4) = 14.322 \pm 0.003 \text{ eV}$ , which was obtained by fitting accurately the appearance threshold of  $\text{CH}_3^+/\text{CH}_4$ , effectively reconciles the very slight difference between the two best previous measurements.<sup>1,2</sup> The principal subject of the paper is the investigation of  $E_{\text{i,ad}}(\text{CH}_3)$ , showing that the ZEKE value<sup>31</sup> is to be preferred over Herzberg's<sup>30</sup> value. The combination of the remeasured  $E_{\text{ap}}$  with the preferred ZEKE  $E_{\text{i,ad}}$  produces  $D_0(\text{H}-\text{CH}_3) = 432.6 \pm 0.3 \text{ kJ mol}^{-1}$ .

(1i) Reexamination of the  $\text{CH}_3^+$  fragment appearance energy from  $\text{CH}_4$  by PFI-PEPICO. The reported value  $E_{\text{ap},0}(\text{CH}_3^+/\text{CH}_4) = 14.323 \pm 0.001 \text{ eV}$  is in excellent agreement with the measurement of Litorja and Ruscic.<sup>8</sup> The quoted uncertainty of  $\pm 0.001 \text{ eV}$  is quite tight and appears to have an intended meaning of 1 s.d., rather than the more customary 95% confidence limit. With the ZEKE value for  $E_{\text{i,ad}}(\text{CH}_3)$  [see (1h) above] this appearance energy yields  $D_0(\text{H}-\text{CH}_3) = 432.7 \pm 0.1 \text{ kJ mol}^{-1}$ .

(1j) BAC-MP4 *ab initio* calculations. The originally quoted uncertainty of  $\pm 5.1 \text{ kJ mol}^{-1}$  was multiplied by a factor of 2 to bring it closer to the desired 95% confidence limit.

(1k) CCSD(T)/cc-pVnZ *ab initio* calculations extrapolated to complete basis set and corrected for core–valence effects produce  $D_0(\text{H}-\text{CH}_3) = 432.6 \text{ kJ mol}^{-1}$  after inclusion of ZPE, which leads to the listed enthalpy of formation. An estimated standard deviation of  $0.3 \text{ kcal mol}^{-1}$  has been quoted by the authors for the sequential set of bond dissociation energies of  $\text{CH}_4$ ; the uncertainty listed in the table corresponds to 2 s.d.

(1l) CBS-Q calculation. The reported average absolute deviation of  $1.57 \text{ kcal mol}^{-1}$  was multiplied by 2 to bring it closer to the desired 95% confidence limit. The equivalent CBS-q and CBS-4 enthalpies of formation are  $145.2 \pm 18$  and  $144.8 \pm 26 \text{ kJ mol}^{-1}$ , where the uncertainties have been obtained in an analogous way.

(1m) G3 *ab initio* calculation. The value listed in the table is converted from  $34.0 \text{ kcal mol}^{-1}$ . The uncertainty quoted in the table corresponds approximately to 95% confidence limits, based on twice the average absolute deviation of  $0.94 \text{ kcal mol}^{-1}$  for the enthalpies in the G2/97 test set, which roughly corresponds to 1 s.d. At the G3(MP2) level of theory<sup>35</sup>  $\Delta_f H^\circ_{298}(\text{CH}_3) = 143.1 \pm 9.9 \text{ kJ mol}^{-1}$  ( $34.2 \text{ kcal mol}^{-1}$ ), where the quoted uncertainty was derived in a similar fashion as for the G3 value. At the G2 level of theory<sup>36</sup>  $\Delta_f H^\circ_{298}(\text{CH}_3) = 146.9 \pm 13.1 \text{ kJ mol}^{-1}$  ( $35.1 \text{ kcal mol}^{-1}$ ).

(1n) W2 *ab initio* calculation. The uncertainty quoted in the table corresponds approximately to 95% confidence limits based on twice the average absolute deviation of  $0.23 \text{ kcal mol}^{-1}$  for the W2 test set, which corresponds roughly to 1 s.d. At the W1 level of theory  $\Delta_f H^\circ_{298}(\text{CH}_3) = 144.6 \pm 3.1 \text{ kJ mol}^{-1}$ , where the uncertainty has been obtained in an analogous way.

(1o) G3(MP2)//B3LYP *ab initio* calculations for 32 selected free radicals. The uncertainty given in the table corresponds approximately to 95% confidence limits based on twice the quoted average absolute deviation of  $3.9 \text{ kJ mol}^{-1}$  for the calculated set of radicals, which corresponds roughly to 1 s.d. Note that the average absolute deviation for all enthalpies in the G2/97 test set using the same method is very slightly larger:<sup>37</sup>  $4.7 \text{ kJ mol}^{-1}$  [see also (1m) above].

(1p) Critical data evaluation, but does not provide a pedigree of the selected value nor does it quote uncertainties; the value seems to correspond to that adopted by JANAF<sup>18</sup> [see (1r) below].

(1q) Recommended value from extensive evaluation of data (mainly kinetic determinations) published until 1981. The selected value for  $\text{CH}_3$  is based primarily on chlorination kinetics of Dobis and Benson.<sup>38</sup> The value listed in the table is converted from  $35.1 \pm 0.2 \text{ kcal mol}^{-1}$ .

(1r) Extensive compilation of thermodynamic data. The  $\text{CH}_3$  properties have been last revised in June 1969. The enthalpy of formation is based on PIMS-PIC determination of Chupka<sup>1</sup> [see (1a) above] coupled to Herzberg's<sup>30</sup>  $E_1(\text{CH}_3)$ . The  $\text{CH}_3$  thermochemical properties have not been revised in the new edition.<sup>39</sup>

(1s) Extensive compilation of thermodynamic data. The selected value is based on PIMS-PIC determination by McCulloh and Dibeler<sup>2</sup> [see (1b) above] coupled to Herzberg's<sup>30</sup>  $E_1(\text{CH}_3)$ . The compilation has also critically analyzed a number of older kinetic measurements.<sup>33,40-46</sup> The value is unchanged from the previous (Russian) edition.<sup>47</sup>

(1t) Critical data evaluation of R-H bond dissociation energies based on three methods: kinetic determinations, positive ion cycle determinations from photoelectron/photoionization measurements, and negative ion cycle determinations from photoelectron measurements of negative ions combined with

gas phase acidities. The recommended value for  $\text{CH}_3$  is from  $D_0(\text{H}-\text{CH}_3) = 432.2 \pm 0.4 \text{ kJ mol}^{-1}$  based on PIMS-PIC by McCulloh and Dibeler<sup>2</sup> [see (1b) above] coupled to Herzberg's<sup>30</sup>  $E_{i,\text{ad}}(\text{CH}_3)$ , and appears in good agreement with KE determination of Seetula *et al.*<sup>6</sup> [see (1f) above]. The value listed in the table is converted from  $35.0 \pm 0.1 \text{ kcal mol}^{-1}$ .

(1u) Critical data evaluation for selected free radicals based on kinetic measurements. The recommended value is an average of five KE determinations<sup>38,4-7</sup> [see (1q) and (1d)-(1g) above].

(1v) The compilation lists theoretical results at various levels of theory, but also makes a reference to one experimental benchmark. The quoted experimental benchmark value is from Gurvich *et al.*<sup>19</sup> [see (1s) above].

(1w) A critical evaluation of enthalpies of formation based on a local thermochemical network consisting of five vertices ( $\text{CH}_3$ ,  $\text{CH}_3^+$ ,  $\text{CH}_2$ ,  $\text{CH}_2^+$ , and ketene) and 14 most accurate measurements (appearance energies, ionization energies, and one calorimetric determination), including measurements from Refs. 1, 2, 8, 9, 30, and 31 [see (1a), (1b), (1h), and (1i) above]. The reported value was produced by a statistical analysis followed by a simultaneous solution of the adjusted network. The value listed in the table is converted from  $35.052 \pm 0.067 \text{ kcal mol}^{-1}$ .

(1x) The tabulation gives a list of compilations as sources, but no specific references for individual species. However, the value appears to correspond to that adopted by the NBS Tables<sup>16</sup> above [see (1p) above] and JANAF<sup>18</sup> tables [see (1r) and (1a) above].

(1y) Thermodynamic data compilation. The tabulation selects  $D_{298}(\text{H}-\text{CH}_3) = 438.9 \pm 0.4 \text{ kJ mol}^{-1}$  citing Berkowitz *et al.*<sup>20</sup> as a source [see (1t) above].

(1z) Critical evaluation of atmospherically relevant kinetic data. Their table of enthalpy data lists Kerr and Stocker<sup>25</sup> [see (1y) above] as their source of  $\Delta_f H^\circ_{298}(\text{CH}_3)$ , who in turn adopt the recommendation of Berkowitz *et al.*<sup>20</sup> [see (1t) above].

(1aa) Thermochemical database for combustion. Burcat quotes Pamidimukkala *et al.*<sup>48</sup> as a source of  $\Delta_f H^\circ_{298}(\text{CH}_3)$ , who have in turn adopted the value given by Baghal-Vayjooee *et al.*<sup>49</sup> of  $\Delta_f H^\circ_{298}(\text{CH}_3) = 35.1 \text{ kcal mol}^{-1}$ .

(1bb) Critical evaluation of atmospherically relevant kinetic data. The quoted value is from Ruscic *et al.*<sup>23</sup> [see (1w) above].

(1cc) An unevaluated tabulation with several values. NIST-JANAF<sup>39</sup> is listed as the first value. The tabulation also lists Tsang's value  $\Delta_f H^\circ_{298}(\text{CH}_3) = 147 \pm 1 \text{ kJ mol}^{-1}$  [see (1u) above].

### Preferred Value of the Enthalpy of Formation

$$\Delta_f H^\circ(298.15 \text{ K}) = 146.7 \pm 0.3 \text{ kJ mol}^{-1}$$

$$\Delta_f H^\circ(0 \text{ K}) = 150.0 \pm 0.3 \text{ kJ mol}^{-1}$$

The photoionization and kinetic results are in very good agreement, although the latter group has more scatter and larger uncertainties. Linear analysis of the data set shows that

all experimental measurements listed above are in mutual agreement within their uncertainties, with the exception of the result of Traeger and McLoughlin.<sup>3</sup> The analysis shows that the latter measurement deviates consistently from all others significantly more than its quoted uncertainty of  $\pm 1.7 \text{ kJ mol}^{-1}$  would suggest, and that reconciliation with the other data can be achieved only if an amplified uncertainty of  $\pm 2.2 \text{ kJ mol}^{-1}$  is assumed.

The preferred value is based on the data analysis using a thermochemical network of Ruscic *et al.*<sup>23</sup> The preferred value can be compared to the weighted average of the PIMSPIC determinations ( $146.7 \pm 0.3 \text{ kJ mol}^{-1}$ , excluding the low result of Traeger and McLoughlin,<sup>3</sup> or  $146.6 \pm 0.5 \text{ kJ mol}^{-1}$ , if that result is included), and to the weighted average of kinetic determinations ( $146.2 \pm 2.2 \text{ kJ mol}^{-1}$ ).

The preferred value corresponds to the C–H bond dissociation energy of methane  $D_0(\text{H}-\text{CH}_3) = 432.72 \pm 0.14 \text{ kJ mol}^{-1}$  ( $439.27 \pm 0.14 \text{ kJ mol}^{-1}$  at 298.15 K), which produces the listed enthalpy when used together with auxiliary thermochemical values from Gurvich *et al.*,<sup>19</sup>  $\Delta_f H^\circ_{298}(\text{CH}_4) = -74.60 \pm 0.30 \text{ kJ mol}^{-1}$ ,  $[H^\circ(298.15 \text{ K}) - H^\circ(0 \text{ K})](\text{CH}_4) = 10.016 \text{ kJ mol}^{-1}$ , and CODATA<sup>50</sup> recommended values  $\Delta_f H^\circ_{298}(\text{H}) = 217.998 \pm 0.006 \text{ kJ mol}^{-1}$ ,  $[H^\circ(298.15 \text{ K}) - H^\circ(0 \text{ K})](\text{H}) = 6.197 \pm 0.001 \text{ kJ mol}^{-1}$ ,  $[H^\circ(298.15 \text{ K}) - H^\circ(0 \text{ K})](\text{C, graphite}) = 1.050 \pm 0.020 \text{ kJ mol}^{-1}$ ,  $[H^\circ(298.15 \text{ K}) - H^\circ(0 \text{ K})](\text{C}) = 6.536 \pm 0.001 \text{ kJ mol}^{-1}$ , and  $[H^\circ(298.15 \text{ K}) - H^\circ(0 \text{ K})](\text{H}_2) = 8.468 \pm 0.001 \text{ kJ mol}^{-1}$ , together with  $[H^\circ(298.15 \text{ K}) - H^\circ(0 \text{ K})](\text{CH}_3) = 10.366 \text{ kJ mol}^{-1}$  as listed below.

Geometry (distance in Å, angles in degrees)<sup>(2a)</sup>

Z matrix		Cartesian coordinates		
		x	y	z
C	C	0.000 000	0.000 000	0.000 000
H 1	H	1.079 000	0.000 000	0.000 000
H 1	H	-0.539 500	0.934 441	0.000 000
H 1	H	-0.539 500	-0.934 441	0.000 000

Moments of inertia in the electronic ground state<sup>(2b)</sup>

$$I_A = I_B = 2.923 \times 10^{-47} \text{ kg m}^2$$

$$I_C = 5.903 \times 10^{-47} \text{ kg m}^2$$

Vibrational wave numbers in the electronic ground state  $\nu_i(\text{cm}^{-1})$ <sup>(2c)</sup>

$$3004.42 (a'_1)$$

$$606.453 (a''_2)$$

$$3160.821 (e')$$

$$1396 (e')$$

T/K	$C_p^\circ(T)$ ( $\text{JK}^{-1} \text{ mol}^{-1}$ )	$S^\circ(T)$ ( $\text{JK}^{-1} \text{ mol}^{-1}$ )	$[H^\circ(T) - H^\circ(0 \text{ K})]$ ( $\text{kJ mol}^{-1}$ )
150	34.105	169.342	5.010
200	35.400	179.323	6.747
250	36.892	187.380	8.554
298.15	38.417	194.008	10.366
300	38.477	194.245	10.437
350	40.120	200.300	12.402
400	41.780	205.765	14.450
500	45.023	215.439	18.791
600	48.100	223.923	23.449
800	53.820	238.557	33.650
1000	58.910	251.127	44.935
1200	63.210	262.260	57.161
1500	68.174	276.929	76.910
2000	73.449	297.336	112.441
2500	76.483	314.081	149.991
3000	78.329	328.202	188.729

## 7-Constant NASA Polynomial

METHYL RADICAL	JUN03 C	1.H	3.	0.	0.G	200.000	6000.000	15.03452	1
0.29781206E+01	0.57978520E-02	-0.19755800E-05	0.30729790E-09	-0.17917416E-13					2
0.16509513E+05	0.47224799E+01	0.36571797E+01	0.21265979E-02	0.54583883E-05					3
-0.66181003E-08	0.24657074E-11	0.16422716E+05	0.16735354E+01	0.17643935E+05					4

## 9-Constant NASA Polynomial

METHYL RADICAL	IUPAC Task Group on Selected Radicals	3 JUN03 C	1.00H	3.00	0.00	0.00	0.00	0.00	15.03452	146700.000
50.000	200.0007	-2.0	-1.0	0.0	1.0	2.0	3.0	4.0	0.0	10366.288
0.118053714D+04	-0.803021345D+02	0.612539341D+01	-0.272411169D-01	0.168957527D-03						
-0.436387090D-06	0.428176848D-09	0.000000000D+00	0.166563130D+05	-0.821195667D+01						
200.000	1000.0007	-2.0	-1.0	0.0	1.0	2.0	3.0	4.0	0.0	10366.288
-0.318321530D+05	0.553269109D+03	-0.456705168D-01	0.143269736D-01	-0.153738893D-04						
0.109219654D-07	-0.326622436D-11	0.000000000D+00	0.138774782D+05	0.215922594D+02						
1000.000	6000.0007	-2.0	-1.0	0.0	1.0	2.0	3.0	4.0	0.0	10366.288
0.268335802D+07	-0.913670211D+04	0.146793592D+02	-0.134271770D-02	0.219685901D-06						
-0.190704534D-10	0.678982878D-15	0.000000000D+00	0.735224540D+05	-0.777538285D+02						

## Comments on Molecular Data, Heat Capacity, Entropy, and Enthalpy Increment

(2a) The geometry reflects  $r_0(\text{CH}) = 1.079 \text{ \AA}$  (rather than  $r_c$ ), congruent with the rotational constant given below [see (2b)]. The rotational constant<sup>51</sup> of  $\text{CD}_3$ ,  $B_0 = 4.802 \text{ cm}^{-1}$ , implies  $r_0(\text{CD}) = 1.078 \text{ \AA}$ .

(2b) The moments of inertia are based on the experimental rotational constants<sup>51</sup>  $B_0 = 9.578 \text{ cm}^{-1}$ , and  $C_0 = 4.742 \text{ cm}^{-1}$ , which were used in the calculations of thermochemical functions. (Note that  $C_0 \neq B_0/2$ , which would be expected under the assumption of a zero inertial defect.)

(2c) The listed vibrational wave numbers are experimentally determined fundamentals.<sup>51</sup>

(2d) The heat capacity, entropy, and enthalpy increment values were calculated in the rigid rotor-harmonic oscillator approximation using the molecular constants given above (note that doubly degenerate vibrations, denoted by  $e'$  after the wave number value, are taken with statistical weight 2 in constructing the partition function).  $S^\circ$  is given for  $p^\circ = 100\,000 \text{ Pa}$  (1 bar). The values listed here differ only slightly from those found in Gurvich *et al.*<sup>19</sup> and in JANAF,<sup>18</sup> which were calculated within the same approximation and using molecular constants that were very similar to those accepted in this evaluation.

(2e) The standard heat capacity, entropy, and enthalpy increment values reported in the NBS Tables<sup>16</sup> are  $C_p^\circ(298.15 \text{ K}) = 38.70 \text{ J mol}^{-1} \text{ K}^{-1}$ ,  $S^\circ(298.15 \text{ K}) = 194.2 \text{ J mol}^{-1} \text{ K}^{-1}$ ,  $H^\circ(298.15 \text{ K}) - H^\circ(0 \text{ K}) = 10.42 \text{ kJ mol}^{-1}$ , in the JANAF<sup>18</sup> and NIST-JANAF<sup>39</sup> thermochemical tables are  $C_p^\circ(298.15 \text{ K}) = 38.693 \text{ J mol}^{-1} \text{ K}^{-1}$ ,  $S^\circ(298.15 \text{ K}) = 194.170 \text{ J mol}^{-1} \text{ K}^{-1}$ ,  $H^\circ(298.15 \text{ K}) - H^\circ(0 \text{ K}) = 10.407 \text{ kJ mol}^{-1}$ , in the compilation by Gurvich *et al.*<sup>19</sup> are  $C_p^\circ(298.15 \text{ K}) = 38.406 \text{ J mol}^{-1} \text{ K}^{-1}$ ,  $S^\circ(298.15 \text{ K}) = 193.957 \text{ J mol}^{-1} \text{ K}^{-1}$ ,  $H^\circ(298.15 \text{ K}) - H^\circ(0 \text{ K}) = 10.365 \text{ kJ mol}^{-1}$ , in the *Thermochemical Database for Combustion*<sup>27</sup> are  $C_p^\circ(298.15 \text{ K}) = 38.412 \text{ J mol}^{-1} \text{ K}^{-1}$ ,  $S^\circ(298.15 \text{ K}) = 193.965 \text{ J mol}^{-1} \text{ K}^{-1}$ , and those obtained from G3MP2B3 computations<sup>15</sup> are  $C_p^\circ(298.15 \text{ K}) = 40.10 \text{ J mol}^{-1} \text{ K}^{-1}$ ,  $S^\circ(298.15 \text{ K}) = 195.62 \text{ J mol}^{-1} \text{ K}^{-1}$ ,  $H^\circ(298.15 \text{ K}) - H^\circ(0 \text{ K}) = 10.68 \text{ kJ mol}^{-1}$ .

## References

- W. A. Chupka, *J. Chem. Phys.* **48**, 2337 (1968).
- K. E. McCulloch and V. H. Dibeler, *J. Chem. Phys.* **64**, 4445 (1976).
- J. C. Traeger and R. G. McLoughlin, *J. Am. Chem. Soc.* **103**, 3647 (1981).
- J. J. Russel, J. A. Seetula, S. M. Senkan, and D. Gutman, *Int. J. Chem. Kinet.* **20**, 759 (1988).
- J. J. Russel, J. A. Seetula, and D. Gutman, *J. Am. Chem. Soc.* **110**, 3092 (1988).
- J. A. Seetula, J. J. Russel, and D. Gutman, *J. Am. Chem. Soc.* **112**, 1347 (1990).
- J. N. Nicovich, C. A. van Dijk, K. D. Kreutter, and P. H. Wine, *J. Phys. Chem.* **95**, 9890 (1991).
- M. Litorja and B. Ruscic, *J. Chem. Phys.* **107**, 9852 (1997).
- K. M. Weitzel, M. Malow, G. K. Jarvis, T. Baer, Y. Song, and C. Y. Ng, *J. Chem. Phys.* **111**, 8267 (1999).
- M. R. Zachariah, P. R. Westmoreland, D. R. Burgess, Jr., W. Tsang, and C. F. Melius, *J. Phys. Chem. A* **100**, 8737 (1996); see also D. R. F. Burgess, Jr., M. R. Zachariah, W. Tsang, and P. R. Westmoreland, *Prog. Energy Combust. Sci.* **21**, 453 (1995).
- K. A. Peterson and T. H. Dunning, Jr., *J. Chem. Phys.* **106**, 4119 (1997).
- L. A. Curtiss, K. Raghavachari, P. C. Redfern, and B. B. Stefanov, *J. Chem. Phys.* **108**, 692 (1998).
- L. A. Curtiss, K. Raghavachari, P. C. Redfern, V. Rassolov, and J. A. Pople, *J. Chem. Phys.* **109**, 7764 (1998).
- S. Parthiban and J. M. L. Martin, *J. Chem. Phys.* **114**, 6014 (2001).
- R. Janoschek and M. J. Rossi, *Int. J. Chem. Kinet.* **34**, 550 (2002).
- D. D. Wagman, W. E. Evans, V. B. Parker, R. H. Schumm, I. Halow, S. M. Bailey, K. L. Churney, and R. L. Nuttall, *The NBS Tables of Chemical Thermodynamic Properties*, *J. Phys. Chem. Ref. Data* **11**, Suppl. 2 (1982).
- D. F. McMillen and D. M. Golden, *Ann. Rev. Phys. Chem.* **33**, 493 (1982).
- M. W. Chase, Jr., C. A. Davies, J. R. Downey, Jr., D. J. Frurip, R. A. McDonald, and A. N. Syverud, *JANAF Thermochemical Tables*, 3rd ed., *J. Phys. Chem. Ref. Data* **14**, Suppl. 1 (1985).
- L. V. Gurvich, I. V. Veyts, and C. B. Alcock, *Thermodynamic Properties of Individual Substances*, 4th ed. (Hemisphere, New York, 1991), Vol. 2.
- J. Berkowitz, G. B. Ellison, and D. Gutman, *J. Phys. Chem.* **98**, 2744 (1994).
- W. Tsang, *Heats of Formation of Organic Free Radicals by Kinetic Methods*, in *Energetics of Organic Free Radicals*, edited by J. A. M. Simoes, A. Greenberg, and J. F. Liebman, *Structure, Energetics and Reactivity in Chemistry (SEARCH) Series* (Chapman and Hall, London, 1996).
- Computational Chemistry Comparison and Benchmark DataBase (CCCBDB), NIST 1999, see <http://srdata.nist.gov/cccbdb/>
- B. Ruscic, M. Litorja, and R. L. Asher, *J. Phys. Chem. A* **103**, 8625 (1999); see also *ibid.* **104**, 8600E (2000).
- Standard Thermodynamic Properties of Chemical Substances*, in *CRC*

- Handbook of Chemistry and Physics*, edited by D. Lide, 82nd ed. (CRC, Boca Raton, FL, 2001–2002).
- <sup>25</sup> J. A. Kerr and D. W. Stocker, *Strengths of Chemical Bonds*, in *CRC Handbook of Chemistry and Physics*, edited by D. Lide, 82nd ed. (CRC, Boca Raton, FL, 2001–2002).
- <sup>26</sup> R. Atkinson, D. L. Baulch, R. A. Cox, R. F. Hampson, Jr., J. A. Kerr, M. J. Rossi, and J. Troe, *J. Phys. Chem. Ref. Data* **29**, 167 (2000).
- <sup>27</sup> A. Burcat, TAE Report No. 867, Technion, Haifa, 2001; see also <ftp://ftp.technion.ac.il/pub/supported/aetdd/thermodynamics>
- <sup>28</sup> S. P. Sander, R. R. Friedl, D. M. Golden, M. J. Kurylo, R. E. Huie, V. L. Orkin, G. K. Moortgat, A. R. Ravishankara, C. E. Kolb, M. J. Molina, and B. J. Finlayson-Pitts, JPL Publication 02-25, NASA and JPL, February 1, 2003.
- <sup>29</sup> H. Y. Afeefy, J. F. Liebman, and S. E. Stein, *Neutral Thermochemical Data*, in *NIST Chemistry WebBook*, NIST Standard Reference Database Number 69, edited by P. J. Linstrom and W. G. Mallard (NIST, Gaithersburg, MD, 2003) (<http://webbook.nist.gov/>)
- <sup>30</sup> G. Herzberg, *Proc. R. Soc. London Ser. A* **262**, 291 (1961).
- <sup>31</sup> J. Blush, P. Chen, R. T. Wiedman, and M. G. White, *J. Chem. Phys.* **98**, 3557 (1993).
- <sup>32</sup> J. B. Pedley and J. Rylance, *Sussex—N.P.L. Computer Analyzed Thermochemical Data: Organic and Organometallic Compounds* (University of Sussex, Press, Sussex, 1977).
- <sup>33</sup> C. A. Goy and H. O. Pritchard, *J. Phys. Chem.* **69**, 3040 (1965).
- <sup>34</sup> J. W. Comber and E. Whittle, *Trans. Faraday Soc.* **62**, 1553 (1966).
- <sup>35</sup> L. A. Curtiss, P. C. Redfern, K. Raghavachari, V. Rassolov, and J. A. Pople, *J. Chem. Phys.* **110**, 4703 (1999).
- <sup>36</sup> L. A. Curtiss, K. Raghavachari, G. W. Trucks, and J. A. Pople, *J. Chem. Phys.* **94**, 7221 (1991).
- <sup>37</sup> A. G. Baboul, L. A. Curtiss, P. C. Redfern, and K. Raghavachari, *J. Chem. Phys.* **110**, 7650 (1999).
- <sup>38</sup> O. Dobis and S. W. Benson, *Int. J. Chem. Kinetics* **19**, 691 (1987).
- <sup>39</sup> M. W. Chase, Jr., *NIST-JANAF Thermochemical Tables*, 4th ed., *J. Phys. Chem. Ref. Data Monogr.* 9 (1998).
- <sup>40</sup> G. B. Kistiakowsky and E. R. van Artsdalen, *J. Chem. Phys.* **12**, 469 (1944).
- <sup>41</sup> M. Szwarc, *Proc. R. Soc. London Ser. A* **198**, 267 (1949).
- <sup>42</sup> G. C. Fettis, J. H. Knox, and A. F. Trotman-Dickenson, *J. Chem. Soc.* **1960**, 4177.
- <sup>43</sup> G. C. Fettis and A. F. Trotman-Dickenson, *J. Chem. Soc.* **1961**, 3037.
- <sup>44</sup> M. C. Flowers and S. W. Benson, *J. Chem. Phys.* **38**, 882 (1963).
- <sup>45</sup> D. M. Golden, R. Walsh, and S. W. Benson, *J. Am. Chem. Soc.* **87**, 4053 (1965).
- <sup>46</sup> N. A. Gac, D. M. Golden, and S. W. Benson, *J. Am. Chem. Soc.* **91**, 3091 (1969).
- <sup>47</sup> V. P. Glushko, L. V. Gurvich, G. A. Bergman, I. V. Veits, V. A. Medvedev, G. A. Khackhuruzov, and V. S. Yungman, *Termodinamicheski Svoistva Individual'nikh Veschestv*, 3rd ed. (Nauka, Moscow, 1979).
- <sup>48</sup> K. M. Pamidimukkala, D. Rogers, and G. B. Skinner, *J. Phys. Chem. Ref. Data* **11**, 83 (1982).
- <sup>49</sup> M. H. Baghal-Vayjooee, A. J. Colussi, and S. W. Benson, *Int. J. Chem. Kinetics* **11**, 147 (1979).
- <sup>50</sup> J. D. Cox, D. D. Wagman, and V. A. Medvedev, *CODATA Key Values for Thermodynamics* (Hemisphere, New York, 1989); see also (<http://www.codata.org/codata/databases/key1.html>)
- <sup>51</sup> M. E. Jacox, *Vibrational and Electronic Energy Levels of Polyatomic Transient Molecules*, *J. Phys. Chem. Ref. Data Monogr.* 3 (1994).

7.1.5. C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub> Radical

## 7.1.5. Benzyl radical

2154-56-5

C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> ( <sup>2</sup> B <sub>1</sub> )	C <sub>2v</sub> (σ <sub>ext</sub> =2)
Δ <sub>f</sub> H°(298.15 K) = 208.0 ± 1.7 kJ mol <sup>-1</sup>	Δ <sub>f</sub> H°(0 K) = 226.8 ± 1.8 kJ mol <sup>-1</sup>
C° <sub>p</sub> (298.15 K) = 109.700 J K <sup>-1</sup> mol <sup>-1</sup>	H°(298.15 K) - H°(0 K) = 18.178 kJ mol <sup>-1</sup>
S°(298.15 K) = 318.229 J K <sup>-1</sup> mol <sup>-1</sup>	p° = 100 000 Pa (1 bar)

## Literature Data for the Enthalpy of Formation at 298.15 K

Δ <sub>f</sub> H°(kJ mol <sup>-1</sup> )	Authors and Reference	Method <sup>a</sup>	Comments
<b>Measurements</b>			
203 ± 6	Walker and Tsang (1990) <sup>1</sup>	ST/KE	(1a)
210.5 ± 4	Hippler and Troe (1990) <sup>2</sup>	ST/KE	(1b)
205.0 ± 6.3	Elmaimouni <i>et al.</i> (1993) <sup>3</sup>	KE	(1c)
207.9 ± 2.5	Ellison <i>et al.</i> (1996) <sup>4</sup>	FA/KE	(1d)
210 ± 8	Song <i>et al.</i> (2002) <sup>5</sup>	ST	(1e)
<b>Computations</b>			
206.6 ± 4.5	Hrovat and Borden (1994) <sup>6</sup>	CASSCF	(1f)
209.4 ± 7.8	Smith and Hall (1997) <sup>7</sup>	G2(MP2,SVP)	(1g)
211.3 ± 5.2 <sup>b</sup>	Henry <i>et al.</i> (2001) <sup>8</sup>	CBS-RAD	(1h)
212.3 ± 7.8 <sup>b</sup>	Janoschek and Rossi (2002) <sup>9</sup>	G3MP2B3	(1i)
206.6 ± 4 <sup>b</sup>	Martin (2003) <sup>10</sup>	W1 <sub>mod</sub>	(1j)
<b>Reviews and Evaluations</b>			
200.0 ± 6.3	McMillen and Golden (1982) <sup>11</sup>	CDE	(1k)
201.3	Hayashibara <i>et al.</i> (1986) <sup>12</sup>	CDE	(1l)
202.5 ± 6.3	Berkowitz <i>et al.</i> (1994) <sup>13</sup>	CDE	(1m)
207 ± 4	Tsang (1996) <sup>14</sup>	CDE	(1n)
207.9 ± 2.5	Kerr and Stocker (2000) <sup>15</sup>	TT-A	(1o)
210.5	Burcat (2001) <sup>16</sup>	TT-A	(1p)
207 ± 4	NIST WebBook (2003) <sup>17</sup>	TT-A	(1q)

<sup>a</sup>KE kinetic equilibrium study; ST shock tube experiment; FA flowing afterglow study; CDE critical data evaluation; TT-A annotated tabulation of thermodynamic data.

<sup>b</sup>The uncertainty was either not given explicitly by the original author(s) or it has been modified; see individual comments for further explanations.

## Comments on the Enthalpies of Formation

(1a) *n*-Pentylbenzene decomposed in single-pulse shock tube experiments over the temperature range of 940–1100 K and pressures of 2–3 atm. Mesitylene is used as chemical inhibitor to inhibit chain processes. The internal standard used in these studies is the decyclization of 4-methylcyclohexene to form equal amounts of propene and 1,3-butadiene for which the rate expression is<sup>18</sup>  $k = 2 \times 10^{15} \exp(-33\,500/T) \text{ s}^{-1}$ . Analysis of the reactants and products is carried out by gas chromatography. The Arrhenius plot for the decomposition reaction, C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub> → C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub> + *n*-C<sub>4</sub>H<sub>9</sub>, leads to the rate expression  $k_f = 1 \times 10^{16} \exp(-36\,500/T) \text{ s}^{-1}$ . Assuming zero activation energy for the combination reaction,  $E_{a,r} = 0 \text{ kJ mol}^{-1}$ , the reaction enthalpy of Δ<sub>f</sub>H°(1100 K) = E<sub>f</sub> + RT = 312.43 kJ mol<sup>-1</sup> is obtained. For *n*-butyl radical, Δ<sub>f</sub>H°(*n*-butyl) = 77 kJ mol<sup>-1</sup> at 300 K and 50.2 kJ mol<sup>-1</sup> at 1100 K is derived from an assumed C–H bond dissociation energy in *n*-butane of 421.5 kJ mol<sup>-1</sup>, obtained as an average of primary C–H bond dissociation energies in ethane and propane. With this and Δ<sub>f</sub>H°<sub>1100</sub>(*n*-pentylbenzene) = -78.2 kJ mol<sup>-1</sup>, the en-

thalpy of formation of Δ<sub>f</sub>H°<sub>1100</sub>(C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>) = 184.1 kJ mol<sup>-1</sup> is derived from the above reaction enthalpy. Finally, with the estimated heat capacity of benzyl, the authors obtain Δ<sub>f</sub>H°<sub>300</sub>(C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>) = 203 kJ mol<sup>-1</sup>.

(1b) The results of measurements of the dissociation and reverse recombination rates of benzyl-containing molecules in shock waves have been used to derive the enthalpy of formation for benzyl radical. The studied systems are: toluene = benzyl + H (1), benzyl iodide = benzyl + I (2) and dibenzyl = 2 benzyl (3). System (1): Previous shock tube measurements on toluene decomposition<sup>19</sup> and the reverse combination<sup>19</sup> gave the equilibrium constant expression of  $K_1 = 5 \exp[-(360 \pm 20) \text{ kJ mol}^{-1}/RT] \text{ mol cm}^{-3}$  over the temperature range 900–1500 K. From this, a third-law enthalpy of formation of Δ<sub>f</sub>H°<sub>298</sub>(C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>) = 210.5 ± 8 kJ mol<sup>-1</sup> is obtained. System (2): Shock tube results<sup>20</sup> gave  $K_2 = 12 \exp(-181 \text{ kJ mol}^{-1}/RT) \text{ mol cm}^{-3}$  for the temperature range 790–950 K from which the third-law value of Δ<sub>f</sub>H°<sub>298</sub>(C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>) = 210.3 kJ mol<sup>-1</sup> is derived. System (3): Shock tube results<sup>20</sup> led to  $K_3 = 160 \exp(-248.1 \text{ kJ mol}^{-1}/RT) \text{ mol cm}^{-3}$ , from which

$\Delta_f H^\circ_{298}(\text{C}_6\text{H}_5\text{CH}_2) = 210.6 \text{ kJ mol}^{-1}$  is obtained. The final result, obtained from these three determinations, is  $\Delta_f H^\circ_{298}(\text{C}_6\text{H}_5\text{CH}_2) = 210.5 \pm 4 \text{ kJ mol}^{-1}$ .

In all three third-law determinations the benzyl radical entropy values of  $S^\circ_T/\text{JK}^{-1}\text{mol}^{-1} = 321.1$  (298.16 K), 540.7 (1000 K) and 650.3 (1500 K), were used which are higher by about  $7 \text{ J mol}^{-1} \text{ K}^{-1}$  than the value calculated by Walker and Tsang<sup>1</sup> using different frequencies and more extensive estimations. In a more recent calculation of the entropy of benzyl radical, Berkowitz *et al.*<sup>13</sup> arrived at  $S^\circ_{1000}(\text{C}_6\text{H}_5\text{CH}_2) = 534.3 \pm 2.7 \text{ J mol}^{-1} \text{ K}^{-1}$ . Recalculating the data with the entropy reported by Berkowitz *et al.* leads to  $\Delta_f H^\circ_{298}(\text{C}_6\text{H}_5\text{CH}_2) = 204.6 \pm 4 \text{ kJ mol}^{-1}$ , in reasonable agreement with Tsang's recommendation.

(1c) The equilibrium  $\text{C}_6\text{H}_5\text{CH}_2 + \text{O}_2 \rightleftharpoons \text{C}_6\text{H}_5\text{CH}_2\text{OO}$  studied between 393 and 433 K using a kinetic method. Flow technique with detection of benzyl radicals by laser induced fluorescence has been used. The radical decay plots were fitted to a double exponential equation which enabled to derive the decay parameters. These supplied the kinetic parameters  $k_f$  and  $k_r$  and the equilibrium constant  $K = k_f/k_r$ . The standard reaction enthalpy,  $\Delta_r H^\circ_{298}$ , has been derived by both second- and third-law analysis. From a modified van't Hoff plot, the second-law values of  $\Delta_r H^\circ_{298} = -(79.1 \pm 5.0) \text{ kJ mol}^{-1}$  and  $\Delta_r S^\circ_{298} = -(105.4 \pm 10.5) \text{ J K}^{-1} \text{ mol}^{-1}$  are obtained. With a standard reaction entropy of  $\Delta_r S^\circ_{298} = -121.3 \text{ J K}^{-1} \text{ mol}^{-1}$ , estimated from additivity rules, a third-law reaction enthalpy of  $\Delta_r H^\circ_{298} = -(85.8 \pm 4.2) \text{ kJ mol}^{-1}$  is derived. On this basis,  $\Delta_r H^\circ_{298} = -(83.7 \pm 4.2) \text{ kJ mol}^{-1}$  is preferred. This, together with an estimated enthalpy of formation for benzylperoxy radical ( $121.3 \text{ kJ mol}^{-1}$ ), leads to the enthalpy of formation of  $\Delta_f H^\circ_{298}(\text{C}_6\text{H}_5\text{CH}_2) = 205.0 \pm 6.3 \text{ kJ mol}^{-1}$ .

(1d) A flowing afterglow/selected ion flow tube instrument<sup>21</sup> is used to measure the rates of reaction  $\text{C}_6\text{H}_5\text{CH}_3 + \text{CH}_3\text{O}^- \rightarrow \text{C}_6\text{H}_5\text{CH}_2^- + \text{CH}_3\text{OH}$ . At  $300 \pm 1 \text{ K}$ , the rate coefficients determined for the forward and reverse reactions were  $k_f = (8.08 \pm 0.13) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  and  $k_r = (6.22 \pm 0.06) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , from which the equilibrium constant  $K(300 \text{ K}) = 1.30 \pm 0.03$  and the reaction free energy change  $\Delta_r G^\circ_{300} = -0.67 \pm 0.08 \text{ kJ mol}^{-1}$  were obtained. The acidity of toluene was derived from this free energy change and the acidity of methanol [taken as  $\Delta_{\text{acid}} G_{300}(\text{CH}_3\text{O}-\text{H}) = 1569.5 \pm 0.8 \text{ kJ mol}^{-1}$ ] by using the relationship  $\Delta_r G^\circ_{300} = \Delta_{\text{acid}} G_{300}(\text{C}_6\text{H}_5\text{CH}_2-\text{H}) - \Delta_{\text{acid}} G_{300}(\text{CH}_3\text{O}-\text{H})$ . Next, with the calculated entropy of deprotonation,  $\Delta_{\text{acid}} S_{300}(\text{C}_6\text{H}_5\text{CH}_2-\text{H}) = 103.3 \pm 6.7 \text{ J K}^{-1} \text{ mol}^{-1}$ ,  $\Delta_{\text{acid}} H_{300}(\text{C}_6\text{H}_5\text{CH}_2-\text{H}) = 1599.6 \pm 2.1 \text{ kJ mol}^{-1}$  was obtained. Finally, the expression  $D_{300}(\text{C}_6\text{H}_5\text{CH}_2-\text{H}) = \Delta_{\text{acid}} H_{300}(\text{C}_6\text{H}_5\text{CH}_2-\text{H}) + E_{\text{ea},0}(\text{C}_6\text{H}_5\text{CH}_2) - E_{\text{i},0}(\text{H}) + [\text{thermal correction}]$  was used to determine the C-H bond dissociation energy in toluene. Combining the value of  $\Delta_{\text{acid}} H_{300}(\text{C}_6\text{H}_5\text{CH}_2-\text{H})$  with the measured electron affinity of benzyl radical<sup>22</sup> the ionization potential of hydrogen atom and thermal correction (estimated to be  $0.12 \pm 0.4 \text{ kJ mol}^{-1}$ ),  $D_{300}(\text{C}_6\text{H}_5\text{CH}_2-\text{H}) = 375.7 \pm 2.5 \text{ kJ mol}^{-1}$  was derived. With an estimated heat capacity correction of

$6.7 \pm 0.8 \text{ kJ mol}^{-1}$ ,  $D_0(\text{C}_6\text{H}_5\text{CH}_2-\text{H}) = 368.6 \pm 2.5 \text{ kJ mol}^{-1}$ , was obtained. These, together with the estimated  $\Delta_f H^\circ_0(\text{C}_6\text{H}_5\text{CH}_3) = 73.6 \pm 1.3 \text{ kJ mol}^{-1}$  lead to the benzyl radical enthalpy of formation of  $\Delta_f H^\circ_0(\text{C}_6\text{H}_5\text{CH}_2) = 226.4 \pm 2.5 \text{ kJ mol}^{-1}$  and  $\Delta_f H^\circ_{300}(\text{C}_6\text{H}_5\text{CH}_2) = 207.9 \pm 2.5 \text{ kJ mol}^{-1}$ .

(1e) The decomposition of benzylamine studied in the temperature range 1225–1599 K and pressure range of 1.19–1.46 bar using shock tube technique. Rice–Ramsperger–Kassel–Marcus (RRKM) calculations were performed in order to obtain the high-pressure-limit rate expression of  $k_\infty = 1.07 \times 10^{16} \exp(-364.70/T) \text{ s}^{-1}$  for the temperature range 100–1600 K. From the results of the RRKM calculations, based on the shock tube results, an activation energy for the C–N bond dissociation in benzylamine at 0 K is derived:  $E_{\text{a},f} = 297.12 \text{ kJ mol}^{-1}$ . A more accurate value of  $E_{\text{a},f} = 305 \pm 4 \text{ kJ mol}^{-1}$  can be obtained from the RRKM analysis of results based on both the shock tube data and the VLPP measurements.<sup>23</sup> Then, the enthalpy of formation of benzyl radical at 0 K,  $\Delta_f H^\circ_0(\text{C}_6\text{H}_5\text{CH}_2) = 228 \pm 5 \text{ kJ mol}^{-1}$ , was derived from the equation  $\Delta_f H^\circ_0(\text{C}_6\text{H}_5\text{CH}_2) = E_{\text{a},f} + \Delta_f H^\circ_0(\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2) - \Delta_f H^\circ_0(\text{NH}_2)$ , using auxiliary data<sup>24,25</sup>  $\Delta_f H^\circ_0(\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2) = 115.5 \pm 2.7 \text{ kJ mol}^{-1}$  and  $\Delta_f H^\circ_0(\text{NH}_2) = 192 \pm 1 \text{ kJ mol}^{-1}$ . Finally, a  $-18 \text{ kJ mol}^{-1}$  integrated heat capacity correction was applied to obtain  $\Delta_f H^\circ_{298}(\text{C}_6\text{H}_5\text{CH}_2) = 210 \pm 5 \text{ kJ mol}^{-1}$ . However, taking into account the assumption of  $0 \text{ kJ mol}^{-1}$  for the reverse reaction (implicit in the derivation) and the difference of the results derived from ST and VLPP experiments, an uncertainty of  $8 \text{ kJ mol}^{-1}$  appears to be more appropriate.

(1f) The isodesmic reaction  $\text{C}_6\text{H}_5\text{CH}_3 + \text{CH}_2:\text{CHCH}_2 \rightarrow \text{C}_6\text{H}_5\text{CH}_2 + \text{CH}_2:\text{CHCH}_3$  studied at various levels of theory. The calculated reaction enthalpy, which corresponds to the difference between the primary C–H bond dissociation energy in toluene and propene, has been found from the complete active space calculations CASSCF/6-31G\*\* and CASPT2N/6-31G\*\* to be 5.9 and 11.7  $\text{kJ mol}^{-1}$ , respectively. On this basis a value of  $D_{298}(\text{C}_6\text{H}_5\text{CH}_2-\text{H}) - D_{298}(\text{CH}_2:\text{CHCH}_2-\text{H}) = 9.5 \pm 3 \text{ kJ mol}^{-1}$  was adopted. Combining this difference with  $D_{298}(\text{CH}_2:\text{CHCH}_2-\text{H}) = 364.9 \pm 2.9 \text{ kJ mol}^{-1}$ ,<sup>26</sup> leads to  $D_{298}(\text{C}_6\text{H}_5\text{CH}_2-\text{H}) = 374.4 \pm 4.2 \text{ kJ mol}^{-1}$ . With  $\Delta_f H^\circ_{298}(\text{C}_6\text{H}_5\text{CH}_3) = 50.17 \pm 0.42 \text{ kJ mol}^{-1}$ ,<sup>27</sup> and  $\Delta_f H^\circ_{298}(\text{H}) = 217.998 \pm 0.006 \text{ kJ mol}^{-1}$ ,<sup>28</sup> one obtains  $\Delta_f H^\circ_{298}(\text{C}_6\text{H}_5\text{CH}_2) = 206.6 \pm 4.5 \text{ kJ mol}^{-1}$ .

(1g) G2(MP2,SVP) calculations to obtain the enthalpy of formation for benzyl radical. Six isogyric reactions have been investigated to obtain the enthalpy of formation  $\Delta_f H^\circ_{298}(\text{C}_6\text{H}_5\text{CH}_2) = 209.4 \pm 7.8 \text{ kJ mol}^{-1}$ , which compares favorably with the value of  $203.8 \text{ kJ mol}^{-1}$  obtained using atomization energies.

(1h) Bond dissociation energies (BDEs) for monosubstituted methyl radicals calculated at a variety of levels including CBS-RAD, G3(MP2)-RAD, and W1. The  $\text{C}_6\text{H}_5\text{CH}_2-\text{H}$



BDEs obtained with G3(MP2)-RAD and CBS-RAD, the two methods which gave results that were generally close to the experimental values, were 367.5 and 377.8 kJ mol<sup>-1</sup>, respectively. From these, one obtains  $D_0(\text{C}_6\text{H}_5\text{CH}_2\text{-H}) = 372.6 \pm 5.2$  kJ mol<sup>-1</sup> which, together with auxiliary thermochemical data,<sup>27,28</sup> lead to  $\Delta_f H^\circ_0(\text{C}_6\text{H}_5\text{CH}_2) = 229.8 \pm 5.2$  kJ mol<sup>-1</sup> and  $\Delta_f H^\circ_{298}(\text{C}_6\text{H}_5\text{CH}_2) = 211.3 \pm 5.2$  kJ mol<sup>-1</sup>.

(1i) G3(MP2)//B3LYP *ab initio* calculations for 32 selected free radicals. The uncertainty given in the table corresponds approximately to 95% confidence limits based on twice the quoted average absolute deviation of 3.9 kJ mol<sup>-1</sup> for the calculated set of radicals, which corresponds roughly to 1 s.d. Note that the average absolute deviation for all enthalpies in the G2/97 test set using the same method is very slightly larger:<sup>29</sup> 4.7 kJ mol<sup>-1</sup>.

(1j) W1 *ab initio* computation, with core correlation and scalar relativistic effects estimated by MSFT bond additivity model<sup>30</sup> based on benzene<sup>31</sup> W1 results. The uncertainty quoted in the table corresponds approximately to 95% confidence limits. It is based on twice the average absolute deviation of 0.37 kcal mol<sup>-1</sup> for the W1 test set,<sup>32</sup> which corresponds roughly to 1 s.d., additionally increased for the fact that some corrections were estimated rather than computed.

(1k) Recommended value from extensive evaluation of data (mainly kinetic determinations) published till 1981. The reported value is based on previous kinetic determinations.

(1l)  $D_{298}(\text{C}_6\text{H}_5\text{CH}_2\text{-H}) = 369.0$  kJ mol<sup>-1</sup> and the corresponding  $\Delta_f H^\circ_{298}(\text{C}_6\text{H}_5\text{CH}_2) = 201.3$  kJ mol<sup>-1</sup> was derived using the relative chloride affinity between  $(\text{CH}_3)_3\text{C}^+$  and  $\text{C}_6\text{H}_5\text{CH}_2^+$  from Sharma *et al.*,<sup>33</sup> the enthalpy of formation of  $(\text{CH}_3)_3\text{CCl}$  and  $\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$  from Cox and Pilcher,<sup>27</sup>  $\Delta_f H^\circ(\text{Cl})$  from the *National Standard Ref. Data Series*,<sup>34</sup> the ionization potential of  $\text{C}_6\text{H}_5\text{CH}_2$  (7.20 eV) from Houle and Beauchamp,<sup>35</sup> and the recommended value of  $\Delta_f H^\circ_{298}(\text{C}(\text{CH}_3)_3^+) = 696.7$  kJ mol<sup>-1</sup> derived from various literature sources.

(1m) Critical data evaluation of R-H bond dissociation energies based on three methods: kinetic determinations, positive ion cycle determinations from photoelectron/photoionization measurements, and negative ion cycle determinations from photoelectron measurements of negative ions combined with gas phase acidities. The recommended value is based on the kinetic equilibrium measurements of Walker and Tsang<sup>1</sup> and Hippler and Troe,<sup>2</sup> reinterpreted by using different entropies than the original authors.

(1n) Critical data evaluation for selected free radicals based on kinetic measurements. The recommended value is based on the results of Walker and Tsang<sup>1</sup> as well as Hippler and Troe.<sup>2</sup>

(1o) Thermodynamic data compilation. The listed value is that reported by Ellison *et al.*<sup>4</sup>

(1p) Thermodynamic database for combustion. The listed value is that reported by Hippler and Troe.<sup>2</sup>

(1q) An unevaluated tabulation of available values from other sources. The listed value is that reported by Tsang.<sup>14</sup>

### Preferred Value of the Enthalpy of Formation

$$\Delta_f H^\circ(298.15 \text{ K}) = 208.0 \pm 1.7 \text{ kJ mol}^{-1}$$

$$\Delta_f H^\circ(0 \text{ K}) = 226.8 \pm 1.8 \text{ kJ mol}^{-1}$$

Part of the spread in the listed values is related to using differing values for auxiliary thermochemical quantities, and particularly for the elevated-temperature values for the entropy of benzyl. In spite of this, the values are still in general agreement within their respective uncertainties. The weighted average of the experimental values,  $\Delta_f H^\circ_{298}(\text{C}_6\text{H}_5\text{CH}_2) = 207.9 \pm 3.0$  kJ mol<sup>-1</sup> differs by only 0.4 kJ mol<sup>-1</sup> from the weighted average of calculations,  $\Delta_f H^\circ_{298}(\text{C}_6\text{H}_5\text{CH}_2) = 208.3 \pm 3.1$  kJ mol<sup>-1</sup>. Hence, the preferred value corresponds to the weighted average of all listed experimental and computed results,  $\Delta_f H^\circ_{298}(\text{C}_6\text{H}_5\text{CH}_2) = 208.0 \pm 1.7$  kJ mol<sup>-1</sup>.

The preferred value corresponds to  $D_{298}(\text{C}_6\text{H}_5\text{CH}_2\text{-H}) = 375.8 \pm 1.7$  kJ mol<sup>-1</sup> ( $369.7 \pm 1.8$  kJ mol<sup>-1</sup> at 0 K). This bond dissociation energy produces the listed enthalpy when used together with auxiliary thermochemical values as follows:  $\Delta_f H^\circ_{298}(\text{C}_6\text{H}_5\text{CH}_3) = 50.17 \pm 0.42$  kJ mol<sup>-1</sup> from Cox and Pilcher,<sup>27</sup>  $[H^\circ(298.15 \text{ K}) - H^\circ(0 \text{ K})](\text{C}_6\text{H}_5\text{CH}_3) = 18.252$  kJ mol<sup>-1</sup> from Ruscic<sup>36</sup> (estimated from scaled frequencies of  $\text{C}_6\text{H}_5\text{CH}_3$  calculated at the B3LYP/6-31G(d) level of theory, and taking the  $\text{CH}_3$  torsion as free internal rotor, as obtained at the same level of theory),  $[H^\circ(298.15 \text{ K}) - H^\circ(0 \text{ K})](\text{C}_6\text{H}_5\text{CH}_2) = 18.178$  kJ mol<sup>-1</sup> as given below, and the CODATA<sup>28</sup> recommended values  $\Delta_f H^\circ_{298}(\text{H}) = 217.998 \pm 0.006$  kJ mol<sup>-1</sup>,  $[H^\circ(298.15 \text{ K}) - H^\circ(0 \text{ K})](\text{H}) = 6.197 \pm 0.001$  kJ mol<sup>-1</sup>,  $[H^\circ(298.15 \text{ K}) - H^\circ(0 \text{ K})](\text{H}_2) = 8.468 \pm 0.001$  kJ mol<sup>-1</sup> and  $[H^\circ(298.15 \text{ K}) - H^\circ(0 \text{ K})](\text{C, graphite}) = 1.050 \pm 0.020$  kJ mol<sup>-1</sup>.

The preferred value implies a benzyl resonance stabilization energy of  $D_{298}(\text{RCH}_2\text{-H}) - D_{298}(\text{C}_6\text{H}_5\text{CH}_2\text{-H}) = 46 \pm 3$  kJ mol<sup>-1</sup>, if  $422 \pm 2$  kJ mol<sup>-1</sup> (see, e.g., ethyl in the present compilation) is taken to represent the prototypical primary C-H bond dissociation energy at 298.15 K in saturated hydrocarbons. Moreover, a radical stabilization energy of  $D_{298}(\text{CH}_3\text{-H}) - D_{298}(\text{C}_6\text{H}_5\text{CH}_2\text{-H}) = 56.6 \pm 1.9$  kJ mol<sup>-1</sup> is obtained with the C-H bond dissociation energy of  $\text{CH}_4$  taken from this compilation.

Geometry (distance in Å, angles in degrees)<sup>(2a)</sup>

Z matrix							Cartesian coordinates			
							x	y	z	
C	1	1.0					C	0.000 000	0.000 000	2.402 343
C	2	1.4068	1	90.0			C	0.000 000	0.000 000	0.995 555
X	3	1.0	2	90.0	1	0.0	C	0.000 000	0.000 000	-1.839 938
C	3	2.8355	4	90.0	2	180.0	C	0.000 000	1.218 018	0.251 895
X	5	1.0	3	90.0	4	0.0	C	0.000 000	-1.218 018	0.251 895
C	3	1.4271	2	121.406	1	90.0	C	0.000 000	1.211 955	-1.133 936
C	3	1.4271	2	121.406	1	-90.0	C	0.000 000	-1.211 955	-1.133 936
C	7	1.3858	3	121.155	2	180.0	H	0.000 000	0.928 199	2.964 500
C	8	1.3858	3	121.155	2	180.0	H	0.000 000	-0.928 199	2.964 500
H	2	1.0852	3	121.201	7	0.0	H	0.000 000	2.160 886	0.793 562
H	2	1.0852	3	121.201	8	0.0	H	0.000 000	-2.160 886	0.793 562
H	7	1.0874	3	118.717	2	0.0	H	0.000 000	2.153 917	-1.676 575
H	8	1.0874	3	118.717	2	0.0	H	0.000 000	-2.153 917	-1.676 575
H	9	1.0871	7	119.694	3	180.0	H	0.000 000	0.000 000	-2.926 247
H	10	1.0871	8	119.694	3	180.0				
H	5	1.0863	6	90.0	3	180.0				

Moments of inertia in the electronic ground state<sup>(2b)</sup>

$$I_A = 151.704 \times 10^{-47} \text{ kg m}^2$$

$$I_B = 311.214 \times 10^{-47} \text{ kg m}^2$$

$$I_C = 462.918 \times 10^{-47} \text{ kg m}^2$$

$$I_r = 2.830 \times 10^{-47} \text{ kg m}^2 \quad (V_2 = 3880 \text{ cm}^{-1}, \sigma_{\text{int}} = 2)$$

Vibrational wave numbers in the electronic ground state  $\nu_i(\text{cm}^{-1})$ <sup>(2c)</sup>

3087 ( $a_1$ )	3070 ( $a_1$ )	3056 ( $a_1$ )	3051 ( $a_1$ )	1555 ( $a_1$ )	1465 ( $a_1$ )
1456 ( $a_1$ )	1248 ( $a_1$ )	1151 ( $a_1$ )	1004 ( $a_1$ )	958 ( $a_1$ )	801 ( $a_1$ )
513 ( $a_1$ )	923 ( $a_2$ )	803 ( $a_2$ )	485 ( $a_2$ , torsion)	378 ( $a_2$ )	947 ( $b_1$ )
862 ( $b_1$ )	744 ( $b_1$ )	675 ( $b_1$ )	657 ( $b_1$ )	463 ( $b_1$ )	195 ( $b_1$ )
3141 ( $b_2$ )	3075 ( $b_2$ )	3058 ( $b_2$ )	1534 ( $b_2$ )	1433 ( $b_2$ )	1313 ( $b_2$ )
1295 ( $b_2$ )	1140 ( $b_2$ )	1083 ( $b_2$ )	944 ( $b_2$ )	604 ( $b_2$ )	343 ( $b_2$ )

Heat Capacity  $C_p^\circ$ , Entropy  $S^\circ$ , and Enthalpy Increment  $[H^\circ(T) - H^\circ(0 \text{ K})]$ <sup>(2d),(2e)</sup>

T(K)	$C_p^\circ(T)$ ( $\text{JK}^{-1} \text{mol}^{-1}$ )	$S^\circ(T)$ ( $\text{JK}^{-1} \text{mol}^{-1}$ )	$[H^\circ(T) - H^\circ(0 \text{ K})]$ ( $\text{kJ mol}^{-1}$ )
150	56.114	263.875	6.002
200	73.023	282.278	9.221
250	91.564	300.547	13.332
298.15	109.700	318.229	18.178
300	110.388	318.910	18.382
350	128.458	337.298	24.358
400	145.168	355.559	31.205
500	173.805	391.146	47.206
600	196.664	424.933	65.772
800	230.276	486.427	108.685
1000	253.664	540.471	157.211
1200	270.494	588.289	209.716
1500	287.645	650.637	293.633
2000	303.786	735.865	441.957
2500	312.200	804.651	596.162
3000	317.011	862.034	753.568



- <sup>8</sup>J. Henry, C. J. Parkinson, P. M. Mayer, and L. Radom, *J. Phys. Chem. A* **105**, 6750 (2001).
- <sup>9</sup>R. Janoschek and M. J. Rossi, *Int. J. Chem. Kinet.* **34**, 550 (2002).
- <sup>10</sup>J. M. L. Martin (private communication, 2003).
- <sup>11</sup>D. F. McMillen and D. M. Golden, *Annu. Rev. Phys. Chem.* **33**, 493 (1982).
- <sup>12</sup>K. Hayashibara, G. H. Kruppa, and J. L. Beauchamp, *J. Am. Chem. Soc.* **108**, 5441 (1986).
- <sup>13</sup>J. Berkowitz, G. B. Ellison, and D. Gutman, *J. Phys. Chem.* **98**, 2744 (1994).
- <sup>14</sup>W. Tsang, *Heats of Formation of Organic Free Radicals by Kinetic Methods*, in *Energetics of Organic Free Radicals*, edited by J. A. M. Simoes, A. Greenberg, and J. F. Liebman, Structure, Energetics and Reactivity in Chemistry (SEARCH) Series (Chapman and Hall, London, 1996).
- <sup>15</sup>J. A. Kerr and D. W. Stocker, *Strengths of Chemical Bonds*, in *CRC Handbook of Chemistry and Physics*, edited by D. Lide Ed., 82nd ed. (CRC, Boca Raton, FL, 2001–2002).
- <sup>16</sup>A. Burcat, TAE Report No. 867, Technion, Haifa, 2001, see also <ftp://ftp.technion.ac.il/pub/supported/aetdd/thermodynamics>
- <sup>17</sup>H. Y. Afeefy, J. F. Liebman, and S. E. Stein, *Neutral Thermochemical Data*, in *NIST Chemistry WebBook*, NIST Standard Reference Database Number 69, edited by P. J. Linstrom and W. G. Mallard (NIST, Gaithersburg, MD, 2003), (<http://webbook.nist.gov/>)
- <sup>18</sup>W. Tsang, *Comparative Rate Single Pulse Shock Tube and the Thermal Stability of Polyatomic Molecules*. In *Shock Waves in Chemistry*, edited by A. Lifshitz (Dekker, New York, 1981), p. 59.
- <sup>19</sup>H. Hippler, C. Reihs, and J. Troe, *Z. Phys. Chem. (Munich)* **167**, 1 (1990).
- <sup>20</sup>W. Müller-Markgraf and J. Troe, *J. Phys. Chem.* **92**, 4899 (1988).
- <sup>21</sup>J. M. Van Doren, S. E. Barlow, C. H. Depuy, and V. M. Bierbaum, *Int. J. Mass Spectrom.* **81**, 85 (1987).
- <sup>22</sup>R. Gunion, M. Gilles, M. Polack, and W. C. Lineberger, *Int. J. Mass Spectrom.* **117**, 621 (1992).
- <sup>23</sup>D. M. Golden, R. K. Solly, N. A. Gac, and S. W. Benson, *J. Am. Chem. Soc.* **94**, 363 (1972).
- <sup>24</sup>A. S. Carson, P. G. Laye, and M. Yurekli, *J. Chem. Thermodyn.* **9**, 827 (1977).
- <sup>25</sup>W. R. Anderson, *J. Phys. Chem.* **93**, 530 (1989).
- <sup>26</sup>W. R. Roth, F. Bauer, A. Beitat, T. Ebbrecht, and M. Wüstefeld, *Chem. Ber.* **124**, 1453 (1991).
- <sup>27</sup>J. D. Cox and G. Pilcher, *Thermochemistry of Organic and Organometallic Compounds* (Academic, New York, 1970).
- <sup>28</sup>J. D. Cox, D. D. Wagman, and V. A. Medvedev, *CODATA Key Values for Thermodynamics* (Hemisphere, New York, 1989); see also (<http://www.codata.org/codata/databases/key1.html>)
- <sup>29</sup>A. G. Baboul, L. A. Curtiss, P. C. Redfern, and K. Raghavachari, *J. Chem. Phys.* **110**, 7650 (1999).
- <sup>30</sup>J. M. L. Martin, A. Sundermann, P. L. Fast, and D. G. Truhlar, *J. Chem. Phys.* **113**, 1348 (2000).
- <sup>31</sup>J. M. L. Martin and G. de Olivera, *J. Chem. Phys.* **111**, 1843 (1999).
- <sup>32</sup>S. Parthiban and J. M. L. Martin, *J. Chem. Phys.* **114**, 6014 (2001).
- <sup>33</sup>R. B. Sharma, D. K. Sen Sharma, K. Hiroaka, and P. Kebarle, *J. Am. Chem. Soc.* **107**, 3747 (1985).
- <sup>34</sup>B. de B. Darwent, *Natl. Stand. Ref. Data Ser. (U.S. Natl. Bur. Stand)* **31**, 25 (1970).
- <sup>35</sup>F. A. Houle and J. L. Beauchamp, *J. Am. Chem. Soc.* **100**, 3290 (1978).
- <sup>36</sup>B. Ruscic (unpublished results, 2003).
- <sup>37</sup>M. E. Jacox, *J. Phys. Chem. Ref. Data* **27**, 115 (1998).
- <sup>38</sup>A. P. Scott and L. Radom, *J. Phys. Chem.* **100**, 16502 (1996).
- <sup>39</sup>F. F. Fenter, B. Nozière, F. Caralp, and R. Lesclaux, *Int. J. Chem. Kinet.* **26**, 171 (1994).

## 7.2. Other Carbon-Centered Radicals

7.2.1. CH<sub>2</sub>OH Radical

## 7.2.1. Hydroxymethyl radical

2597-43-5

CH <sub>2</sub> OH( <sup>2</sup> A[ <sup>2</sup> A''])	C <sub>1</sub> [C <sub>s</sub> ](σ <sub>ext</sub> =1)
Δ <sub>f</sub> H°(298.15 K) = -17.0 ± 0.7 kJ mol <sup>-1</sup>	Δ <sub>f</sub> H°(0 K) = -10.7 ± 0.7 kJ mol <sup>-1</sup>
C <sup>o</sup> <sub>p</sub> (298.15 K) = 47.401 J K <sup>-1</sup> mol <sup>-1</sup>	H°(298.15 K) - H°(0 K) = 11.781 kJ mol <sup>-1</sup>
S°(298.15 K) = 244.170 J K <sup>-1</sup> mol <sup>-1</sup>	p° = 100 000 Pa (1 bar)

## Literature Data for the Enthalpy of Formation at 298.15 K

Δ <sub>f</sub> H°(kJ mol <sup>-1</sup> )	Authors and Reference	Method <sup>a</sup>	Comments
<b>Measurements</b>			
-15.9 <sup>b</sup> ± 3.1 <sup>c</sup>	Dyke <i>et al.</i> (1984) <sup>1</sup>	PES-PIC	(1a)
-24 ± 8 <sup>c</sup>	Holmes and Lossing (1984) <sup>2</sup>	EIMS-PIC	(1b)
≤ -14.9 <sup>b</sup> ± 2.9	Ruscic and Berkowitz (1991) <sup>3</sup>	PIMS-PIC	(1c)
-8.9 ± 1.8	Seetula and Gutman (1992) <sup>4</sup>	KE	(1d)
-9 ± 6	Dóbe <i>et al.</i> (1993) <sup>5</sup>	KE	(1e)
-18.6 <sup>b</sup> ± 1.1 <sup>c</sup>	Traeger and Holmes (1993) <sup>6</sup>	PIMS-PIC	(1f)
-16.9 <sup>b</sup> ± 0.9	Ruscic and Berkowitz (1993) <sup>7</sup>	PIMS-PIC	(1g)
-16.6 ± 1.3	Dóbe <i>et al.</i> (1996) <sup>8</sup>	KE	(1h)
-17.3 <sup>b</sup> ± 0.9	Litorja and Ruscic (1998) <sup>9</sup>	PIMS-PIC	(1i)
<b>Computations</b>			
-17.3 <sup>b</sup> ± 6.3	Sana and Leroy (1991) <sup>10</sup>	MP4	(1j)
-21.8 <sup>b</sup>	Pardo <i>et al.</i> (1992) <sup>11</sup>	MP4	(1k)
-10.0 <sup>b</sup> ± 8.4	Bauschlicher <i>et al.</i> (1992) <sup>12</sup>	MCPF	(1l)
-15.6 ± 3 <sup>c</sup>	Espinoza-Garcia and Olivares del Valle (1993) <sup>13</sup>	MP4	(1m)
-15.2 ± 3.5	Bauschlicher and Partridge (1994) <sup>14</sup>	CCSD(T)	(1n)
-19.5 ± 9.2 <sup>c</sup>	Zachariah <i>et al.</i> (1996) <sup>15</sup>	BAC-MP4	(1o)
-18.4 ± 2.6 <sup>c</sup>	Johnson and Hudgens (1996) <sup>16</sup>	CBS-QCI/APNO	(1p)
-15.9 ± 13 <sup>c</sup>	Curtiss <i>et al.</i> (1998) <sup>17</sup>	CBS-Q	(1q)
-16.3 ± 7.9 <sup>c</sup>	Curtiss <i>et al.</i> (1998) <sup>18</sup>	G3	(1r)
-19.7 ± 3.1 <sup>c</sup>	Parthiban and Martin (2001) <sup>19</sup>	W1	(1s)
-15.7 <sup>b</sup> ± 3 <sup>c</sup>	Henry <i>et al.</i> (2001) <sup>20</sup>	CBS-RAD	(1t)
-16.4 ± 7.8 <sup>c</sup>	Janoschek and Rossi (2002) <sup>21</sup>	G3MP2B3	(1u)
-16.9 ± 0.7	Marenich and Boggs (2003) <sup>22</sup>	CCSD(T)	(1v)
<b>Reviews and Evaluations</b>			
-25.9 ± 6.3	McMillen and Golden (1982) <sup>23</sup>	CDE	(1w)
-20 ± 10	Gurvich <i>et al.</i> (1991) <sup>24</sup>	CDE	(1x)
-20.4	Kuo <i>et al.</i> (1994) <sup>25</sup>	CDE	(1y)
-17.1 ± 3.3	Berkowitz <i>et al.</i> (1994) <sup>26</sup>	CDE	(1z)
-17.8 ± 1.3	Johnson and Hudgens (1996) <sup>16</sup>	CDE	(1aa)
-9 ± 4	Tsang (1996) <sup>27</sup>	CDE	(1bb)
-18.8 ± 1.3	Traeger and Kompe (1996) <sup>28</sup>	CDE	(1cc)
-17.8 ± 2.6	NIST CCCBDB (1999) <sup>29</sup>	TT-A	(1dd)
-17.8 ± 1.3	Atkinson <i>et al.</i> , (2000) <sup>30</sup>	TT-A	(1ee)
-17.8 ± 1.3	Kerr and Stocker (2001) <sup>31</sup>	TT-A	(1ff)
-17.8 ± 1.3	Burcat (2001) <sup>32</sup>	TT-A	(1gg)
-11.5 ± 1.3	Sander <i>et al.</i> (2003) <sup>33</sup>	TT-A	(1hh)
-9.0 ± 4.0	NIST WebBook (2001) <sup>34</sup>	TT-A	(1ii)

<sup>a</sup>PES-PIC: positive ion cycle based on combining the ionization energy, derived by using photoelectron spectroscopy, with the enthalpy of formation of the appropriate cation; EIMS-PIC: positive ion cycle based on combining electron impact mass-spectrometric measurements of appearance energy ( $E_{ap}$ ) from a stable molecule with ionization energy ( $E_i$ ) of the radical; PIMS-PIC: positive ion cycle based on combining photoionization measurements of fragment appearance energy from a stable molecule with ionization energy of the radical; KE: kinetic equilibrium study; CDE: critical data evaluation; and TT-A: annotated tabulation of thermodynamic data.

<sup>b</sup>The quoted value was either not given explicitly by the author(s) or it was recalculated using auxiliary thermochemical values that differ from those used by the original authors; see individual comments for additional details.

<sup>c</sup>The uncertainty was either not given explicitly by the original author(s) or it has been modified; see individual comments for further explanations.

### Comments on the Enthalpies of Formation

(1a) Vacuum ultraviolet photoelectron spectroscopy study. The adiabatic ionization energy of  $\text{CH}_2\text{OH}$  was measured to be  $E_{i,\text{ad}}(\text{CH}_2\text{OH}) = 7.56 \pm 0.01$  eV. The suggested enthalpy of formation,  $\Delta_f H^\circ_{298}(\text{CH}_2\text{OH}) = -0.25 \pm 0.13$  eV ( $= -24 \pm 13$  kJ mol $^{-1}$ ), was obtained by combining this ionization energy with the enthalpy of formation of  $\text{CH}_2\text{OH}^+$ , quoted by the authors as  $\Delta_f H^\circ_{298}(\text{CH}_2\text{OH}^+) = 7.3 \pm 0.12$  eV ( $= 704 \pm 12$  kJ mol $^{-1}$ ). The latter was apparently derived from the proton affinity of formaldehyde by Tanaka *et al.*<sup>35</sup> However, while Tanaka *et al.* investigated the proton affinities of  $\text{H}_2\text{O}$ ,  $\text{H}_2\text{S}$ ,  $\text{HCN}$ , and  $\text{H}_2\text{CO}$ , they did not determine the proton affinity of formaldehyde; instead, they measured the proton affinities of the other three molecules *relative* to formaldehyde, which they took as known, based on  $\Delta_f H^\circ_{298}(\text{CH}_2\text{OH}^+) = 712.5 \pm 4.6$  kJ mol $^{-1}$  as obtained by Refaey and Chupka<sup>36</sup> in a photoionization study of the fragment appearance energy of  $\text{CH}_2\text{OH}^+$  from  $\text{CH}_3\text{OH}$ . Taking a more direct route than that chosen by Dyke *et al.*<sup>1</sup> and combining the value for  $E_{\text{ap},0}(\text{CH}_2\text{OH}^+/\text{CH}_3\text{OH}) = 11.67 \pm 0.03$  eV given by Refaey and Chupka<sup>1</sup> with  $E_{i,\text{ad}}(\text{CH}_2\text{OH}) = 7.56 \pm 0.01$  eV leads to a C–H bond dissociation energy of methanol at 0 K of  $D_0(\text{H}-\text{CH}_2\text{OH}) = 396.6 \pm 3.1$  kJ mol $^{-1}$ . With the help of auxiliary thermochemical quantities,  $\Delta_f H^\circ_{298}(\text{H}) = 217.998 \pm 0.006$  kJ mol $^{-1}$  and  $[H^\circ(298.15 \text{ K}) - H^\circ(0 \text{ K})](\text{H}) = 6.197$  kJ mol $^{-1}$ , as recommended by CODATA,<sup>37</sup>  $\Delta_f H^\circ_{298}(\text{CH}_3\text{OH}) = -201.0 \pm 0.6$  kJ mol $^{-1}$  and  $[H^\circ(298.15 \text{ K}) - H^\circ(0 \text{ K})](\text{CH}_3\text{OH}) = 11.441$  kJ mol $^{-1}$  from Gurvich *et al.*,<sup>24</sup> and  $[H^\circ(298.15 \text{ K}) - H^\circ(0 \text{ K})](\text{CH}_2\text{OH}) = 11.781$  kJ mol $^{-1}$ , as arising from the study of Johnson and Hudgens<sup>16</sup> [see (1p) below] and adopted in the present evaluation [see (2c) below], this results in  $D_{298}(\text{H}-\text{CH}_2\text{OH}) = 403.1 \pm 3.1$  kJ mol $^{-1}$  and  $\Delta_f H^\circ_{298}(\text{CH}_2\text{OH}) = -15.9 \pm 3.1$  kJ mol $^{-1}$ , which is the value given in the table.

(1b) Electron impact mass-spectrometric measurements of appearance energies. The reported enthalpy of formation for  $\text{CH}_2\text{OH}$  was derived from the determination of the electron-impact appearance energies  $E_{\text{ap}}(\text{CH}_2\text{OH}^+/\text{HOCH}_2\text{CH}_2\text{OH}) = 11.12 \pm 0.05$  eV,  $E_{\text{ap}}(\text{CH}_3\text{CHOH}^+/\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{OH}) = 10.16 \pm 0.05$  eV and  $E_{\text{ap}}(\text{CH}_2\text{NH}_2^+/\text{H}_2\text{NCH}_2\text{CH}_2\text{OH}) = 9.49 \pm 0.05$  eV combined with the literature electron-impact values<sup>38,39</sup> of  $\Delta_f H^\circ(\text{CH}_2\text{OH}^+) = 707$  kJ mol $^{-1}$ ,  $\Delta_f H^\circ(\text{CH}_3\text{CHOH}^+) = 582$  kJ mol $^{-1}$ , and  $\Delta_f H^\circ(\text{CH}_2\text{NH}_2^+) = 741$  kJ mol $^{-1}$ , together with enthalpies of formation for the parent compounds that are either tabulated<sup>40</sup> or estimated from group additivity. The reported enthalpy of formation,  $-23.8$  kJ mol $^{-1}$  ( $-5.7$  kcal mol $^{-1}$ ), is the average of the derived values of  $-5.2$ ,  $-5.4$ , and  $-6.4$  kcal mol $^{-1}$ . The authors do not give an explicit uncertainty estimate. The presently assigned uncertainty reflects the disparity between the three measurements.

(1c) Photoionization mass spectrometry study of  $\text{CD}_2\text{OH}$  to obtain the adiabatic ionization energy  $E_{i,\text{ad}}(\text{CD}_2\text{OH}) = 7.540 \pm 0.006$  eV; after an estimated correction of 0.010 eV for the isotope effect,  $E_{i,\text{ad}}(\text{CH}_2\text{OH}) = 7.550 \pm 0.006$  eV. An enthalpy of formation of  $\Delta_f H^\circ_{298}(\text{CH}_2\text{OH}^+) \leq 719.7$

$\pm 2.9$  kJ mol $^{-1}$  was obtained using the photoionization fragment appearance energy of  $\text{CH}_2\text{OH}^+$  from  $\text{CH}_3\text{OH}$  measured by Refaey and Chupka,<sup>36</sup>  $E_{\text{ap},0}(\text{CH}_2\text{OH}^+/\text{CH}_3\text{OH}) = 11.67 \pm 0.03$  eV in a study of the photodissociative ionization appearance potential of  $\text{CH}_2\text{OH}^+$  from  $\text{CH}_3\text{OH}$ . Finally,  $\Delta_f H^\circ_{298}(\text{CH}_2\text{OH}) \leq -8.8 \pm 2.9$  kJ mol $^{-1}$  was deduced from the ionization energy of  $\text{CH}_2\text{OH}$  and the enthalpy of formation of  $\text{CH}_2\text{OH}^+$  and converted to  $\Delta_f H^\circ_{298}(\text{CH}_2\text{OH}) \leq -15.5 \pm 2.9$  kJ mol $^{-1}$ . The value  $E_{i,\text{ad}}(\text{CH}_2\text{OH}) = 7.550 \pm 0.006$  eV, when combined with  $E_{\text{ap},0}(\text{CH}_2\text{OH}^+/\text{CH}_3\text{OH})$  given by Refaey and Chupka<sup>36</sup> and treated as an upper limit, leads to a C–H bond dissociation energy of methanol at 0 K of  $D_0(\text{H}-\text{CH}_2\text{OH}) \leq 397.5 \pm 2.9$  kJ mol $^{-1}$ . With the help of auxiliary thermochemical quantities given in (1a) above, this results in  $D_{298}(\text{H}-\text{CH}_2\text{OH}) \leq 404.1 \pm 2.9$  kJ mol $^{-1}$  and  $\Delta_f H^\circ_{298}(\text{CH}_2\text{OH}) \leq -14.9 \pm 2.9$  kJ mol $^{-1}$ , which is the value given in the table.

(1d) Reactions  $\text{CH}_2\text{OH} + \text{HBr} \rightarrow \text{CH}_3\text{OH} + \text{Br}$  and  $\text{CH}_2\text{OH} + \text{HI} \rightarrow \text{CH}_3\text{OH} + \text{I}$  studied using excimer laser flash photolysis coupled with time-resolved photoionization mass spectrometry.

Reaction  $\text{CH}_2\text{OH} + \text{HBr} \rightarrow \text{CH}_3\text{OH} + \text{Br}$  was investigated over the temperature range of 298–538 K giving  $k_f = (8.7 \pm 3.2) \times 10^{-13} \exp[(3.7 \pm 1.3) \text{ kJ mol}^{-1}/RT]$  cm $^3$  molecule $^{-1}$  s $^{-1}$  for the forward reaction. The equilibrium constant at 349 K was derived from  $k_f$  and the 394 K reverse reaction rate coefficient  $k_r = (1.03 \pm 0.28) \times 10^{-16}$  cm $^3$  molecule $^{-1}$  s $^{-1}$ , which was obtained by recalculation of the experimental data of Buckley and Whittle.<sup>41</sup> A third-law enthalpy of formation of  $\text{CH}_2\text{OH}$  was derived from the equilibrium constant by using tabulated thermodynamic properties.<sup>42,43</sup>

Reaction  $\text{CH}_2\text{OH} + \text{HI} \rightarrow \text{CH}_3\text{OH} + \text{I}$  was investigated over the temperature range of 298–538 K, giving  $k_f = (2.7 \pm 0.5) \times 10^{-1} \exp[(4.8 \pm 10.5) \text{ kJ mol}^{-1}/RT]$  cm $^3$  molecule $^{-1}$  s $^{-1}$  for the forward reaction. This was combined with the rate coefficient expression  $k_r = 10^{11.5 \pm 0.7} \exp[(-26 \pm 1.8) \text{ kJ mol}^{-1}/RT]$  dm $^3$  mol $^{-1}$  s $^{-1}$ , reported by Cruickshank and Benson<sup>44</sup> for the reverse reaction, to obtain (with tabulated thermodynamic properties<sup>42,43</sup>) the second-law ( $-8.7 \pm 7.6$  kJ mol $^{-1}$ ) and third-law ( $-8.1 \pm 8.0$  kJ mol $^{-1}$ ) values for the standard enthalpy of formation of  $\text{CH}_2\text{OH}$ .

The entropy used in the third-law determinations,  $S^\circ_{298}(\text{CH}_2\text{OH}) = 255.55$  J mol $^{-1}$  K $^{-1}$ , was taken from a compilation of Tsang<sup>42</sup> which is obtained from a calculation treating one of the internal modes as a free rotation. Later studies did not, however, justify such a treatment.<sup>45</sup> This entropy differs considerably from the value of  $S^\circ_{298}(\text{CH}_2\text{OH}) = 244.170 \pm 0.018$  J mol $^{-1}$  K $^{-1}$  given recently by Johnson and Hudgens<sup>16</sup> [see (1p) below], and adopted in the current evaluation [see (2c) below]. If the latter entropy and the corresponding heat capacity for  $\text{CH}_2\text{OH}$  are used, third-law enthalpies of formation lowered by about 5 kJ mol $^{-1}$  are obtained.<sup>16</sup>

The value recommended by the authors and listed in the table is a weighted average of the two third-law and one

second-law determinations of the enthalpy of formation of the  $\text{CH}_2\text{OH}$  radical.

(1e) The kinetics of methanol chlorination equilibrium,  $\text{CH}_2\text{OH} + \text{HCl} = \text{CH}_3\text{OH} + \text{Cl}$ , studied using the fast flow technique with laser magnetic resonance and electron paramagnetic resonance detection. The rate coefficients were found to be  $k_f = (3.8 \pm 1.5) \times 10^{-13} \exp[(20.9 \pm 2.9) \text{ kJ mol}^{-1}/RT] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (at 50–815 K) for the forward reaction and  $k_r = (6.17 \pm 0.67) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (at 298.15 K) for the reverse reaction. These kinetic results were used in the second-law and third-law derivations of the  $\text{CH}_2\text{OH}$  enthalpy of formation. In the second-law determination,  $E_{\text{a,f}} = 20.9 \pm 2.9 \text{ kJ mol}^{-1}$  and an assumed value of  $E_{\text{a,r}} = (0 \pm 4) \text{ kJ mol}^{-1}$ , together with known enthalpies of formation of the other reactants,<sup>42</sup> gave  $\Delta_f H^\circ_{298}(\text{CH}_2\text{OH}) = -8.5 \pm 5.1 \text{ kJ mol}^{-1}$ . In the third-law determination, an equilibrium constant at 298.15 K was calculated from the kinetic results:  $K = k_f/k_r$ . Using this value, an estimated entropy of  $S^\circ_{298}(\text{CH}_2\text{OH}) = 254 \pm 4 \text{ kJ mol}^{-1} \text{ K}^{-1}$  as well as tabulated thermodynamic properties for the other species involved in the reaction<sup>43</sup> gave the third-law result of  $\Delta_f H^\circ_{298}(\text{CH}_2\text{OH}) = -10 \pm 5 \text{ kJ mol}^{-1}$ . As in (1d) above, the estimated entropy of  $\text{CH}_2\text{OH}$  used in the derivation differs considerably from the presently accepted value of  $S^\circ_{298}(\text{CH}_2\text{OH}) = 244.170 \pm 0.018 \text{ J mol}^{-1} \text{ K}^{-1}$ , which was given recently by Johnson and Hudgens<sup>16</sup> [see (1p) and (2c) below]. If this entropy and the corresponding heat capacity for  $\text{CH}_2\text{OH}$  are used, a hydroxymethyl radical enthalpy of formation lower by  $\sim 3 \text{ kJ mol}^{-1}$  is obtained.<sup>16</sup>

The enthalpy of formation of the  $\text{CH}_2\text{OH}$  radical recommended by the authors and listed in the table is the weighted average of the second-law and third-law determinations.

(1f) Photoionization mass spectrometry used to obtain the appearance energy for  $\text{CH}_2\text{OH}^+$  from methanol by linear extrapolation:  $E_{\text{ap},298}(\text{CH}_2\text{OH}^+/\text{CH}_3\text{OH}) = 11.578 \pm 0.007 \text{ eV}$ . The approach of Traeger and Holmes applies all the necessary thermal transformations from 298.15 to 0 K in one step, without explicitly giving  $E_{\text{ap},0}$  values.<sup>46</sup> From the appearance energy, they obtain  $\Delta_f H^\circ_{298}(\text{CH}_2\text{OH}^+) = 708.5 \pm 0.8 \text{ kJ}$  by using  $\Delta_f H^\circ_{298}(\text{CH}_3\text{OH}) = -201.5 \pm 0.3$  from Pedley *et al.*<sup>47</sup> and other auxiliary enthalpies of formation and thermal energy corrections.<sup>43,46</sup> With the ionization energy of  $\text{CH}_2\text{OH}$  of Ruscic and Berkowitz<sup>3</sup> and with additional thermal corrections<sup>43,46</sup> they obtain  $\Delta_f H^\circ_{298}(\text{CH}_2\text{OH}) = -18.9 \pm 1.0 \text{ kJ mol}^{-1}$ . These authors also proposed that previous kinetic data<sup>4</sup> [see (1d) and also (1e) above] can be brought in better accord with photoionization data if the internal rotation in  $\text{CH}_2\text{OH}$  is treated as a pseudovibration, rather than as free rotation. Based on the enthalpy increment of the parent methanol molecule,  $[H^\circ(298.15 \text{ K}) - H^\circ(0 \text{ K})](\text{CH}_3\text{OH}) = 11.441 \text{ kJ mol}^{-1}$  from Gurvich *et al.*,<sup>24</sup> the expected thermal shift of the appearance energy threshold of a fragment ion from  $\text{CH}_3\text{OH}$  at 298.15 K is 0.0543 eV. Hence, from the reported  $E_{\text{ap},298}(\text{CH}_2\text{OH}^+/\text{CH}_3\text{OH}) = 11.578 \pm 0.007 \text{ eV}$  one obtains  $E_{\text{ap},0}(\text{CH}_2\text{OH}^+/\text{CH}_3\text{OH}) = 11.632 \pm 0.007 \text{ eV}$ . With the ionization energy of  $\text{CH}_2\text{OH}$  of Ruscic and Berkowitz,<sup>3</sup> this

results in  $D_0(\text{H}-\text{CH}_2\text{OH}) = 393.9 \pm 0.9 \text{ kJ mol}^{-1}$ , or, with auxiliary thermochemical quantities as given in (1a) above,  $D_{298}(\text{H}-\text{CH}_2\text{OH}) = 400.4 \pm 0.9 \text{ kJ mol}^{-1}$  and  $\Delta_f H^\circ_{298}(\text{CH}_2\text{OH}) = -18.6 \pm 1.1 \text{ kJ mol}^{-1}$ , which is the value given in the table.

(1g) The photoionization mass spectrometric appearance energy of  $\text{CH}_2\text{OH}^+$  from  $\text{CH}_3\text{OH}$  remeasured and determined by accurate fitting to be  $E_{\text{ap},0}(\text{CH}_2\text{OH}^+/\text{CH}_3\text{OH}) = 11.649 \pm 0.003 \text{ eV}$ . The authors show that the linear extrapolation of Traeger and Holmes<sup>6</sup> [see (1f) above] results in an appearance energy that is too low. They also address the persisting discrepancy between previous kinetic data<sup>4</sup> and photoionization data, and suggest that previous treatments of the internal rotation in  $\text{CH}_2\text{OH}$  either underestimate [free rotor approach<sup>42</sup> used in earlier kinetic studies, see (1d) and also (1e) above] or overestimate [pseudo-vibration approach,<sup>6</sup> see (1f) above] the relevant contribution to the entropy, and use a hindered rotor treatment in an attempt to reconcile the kinetic data [see (1z) below for further developments on this subject]. The redetermined fragment appearance energy, together with the reported ionization energy<sup>3,48</sup> of  $E_{\text{i,ad}}(\text{CH}_2\text{OH}) = 7.549 \pm 0.006 \text{ eV}$ , results in  $D_0(\text{H}-\text{CH}_2\text{OH}) = 395.6 \pm 0.6 \text{ kJ mol}^{-1}$  and  $D_{298}(\text{H}-\text{CH}_2\text{OH}) = 402.3 \pm 0.6 \text{ kJ mol}^{-1}$ . The conversion to 298.15 K uses an improved enthalpy increment for  $\text{CH}_2\text{OH}$  that is based on hindered rotor approach mentioned above. With auxiliary thermochemical quantities<sup>24</sup> the authors obtain  $\Delta_f H^\circ_0(\text{CH}_2\text{OH}) = -10.5 \pm 0.9 \text{ kJ mol}^{-1}$  or  $\Delta_f H^\circ_{298}(\text{CH}_2\text{OH}) = -16.6 \pm 0.9 \text{ kJ mol}^{-1}$ . The presently adopted auxiliary thermochemical quantities [see (1a) above] lead to slightly different 298.15 K values:  $D_{298}(\text{H}-\text{CH}_2\text{OH}) = 402.1 \pm 0.6 \text{ kJ mol}^{-1}$  and  $\Delta_f H^\circ_{298}(\text{CH}_2\text{OH}) = -16.9 \pm 0.9 \text{ kJ mol}^{-1}$ , which is the value listed in the table.

(1h) The chemical equilibrium  $\text{Br} + \text{CH}_3\text{OH} = \text{HBr} + \text{CH}_2\text{OH}$  studied by investigating the kinetics of the forward and reverse reactions. Excimer laser photolysis with Br atom resonance fluorescence detection was used over the temperature range of 439–713 K to obtain  $k_f = (5.68 \pm 1.48) \times 10^{-15} T^{1.5} \exp[-(29.93 \pm 1.47) \text{ kJ mol}^{-1}/RT] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . Fast flow technique with laser magnetic resonance for monitoring the  $\text{CH}_2\text{OH}$  radicals was used over the temperature range of 220–473 K to obtain  $k_r = (2.00 \pm 0.42) \times 10^{-12} \exp[(3.24 \pm 0.44) \text{ kJ mol}^{-1}/RT] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .

Activation energies of  $E_{\text{a,f}} = 35.5 \pm 1.47 \text{ kJ mol}^{-1}$  and  $E_{\text{a,r}} = -3.24 \pm 0.44 \text{ kJ mol}^{-1}$  together with auxiliary thermodynamic values<sup>16,43,49</sup> (molar heat capacities and enthalpies of formation) gave the second-law enthalpy of formation of  $\Delta_f H^\circ_{298}(\text{CH}_2\text{OH}) = -15.54 \pm 1.56 \text{ kJ mol}^{-1}$ .

A third-law value was derived from the 450 K equilibrium constant calculated from the kinetic expressions given above. With the molar heat capacities and entropy of  $\text{CH}_2\text{OH}$  as given by Johnson and Hudgens<sup>16</sup> (corresponding to  $S^\circ_{298}(\text{CH}_2\text{OH}) = 244.170 \pm 0.018 \text{ J mol}^{-1} \text{ K}^{-1}$ ) and with thermodynamic properties<sup>43,49</sup> for the other species involved

in the equilibrium, the enthalpy of formation of  $\Delta_f H^\circ_{298}(\text{CH}_2\text{OH}) = -18.84 \pm 2.12 \text{ kJ mol}^{-1}$  was derived.

The value recommended by the authors and listed in the table was obtained as the weighted average of the second-law and third-law determinations.

(li) The authors point out that the adiabatic ionization energy of  $\text{CH}_2\text{OH}$  was misreported<sup>7,48</sup> as  $7.549 \pm 0.006 \text{ eV}$  by erroneous conversion from wavelength to energy, and that the proper value should have been  $E_{i,\text{ad}}(\text{CH}_2\text{OH}) = 7.553 \pm 0.006 \text{ eV}$ . [See also (1y) below.] They combine the corrected ionization energy with the fitted appearance threshold  $E_{\text{ap},0}(\text{CH}_2\text{OH}^+/\text{CH}_3\text{OH}) = 11.649 \pm 0.003 \text{ eV}$  to obtain directly  $D_0(\text{H}-\text{CH}_2\text{OH}) = 395.2 \pm 0.6 \text{ kJ mol}^{-1}$  and, with auxiliary thermochemical values from Gurvich *et al.*,<sup>24</sup>  $\Delta_f H^\circ_0(\text{CH}_2\text{OH}) = -10.95 \pm 0.85 \text{ kJ mol}^{-1}$ . With the currently adopted auxiliary thermochemical values [see (1a) above], these 0 K values correspond to  $D_{298}(\text{H}-\text{CH}_2\text{OH}) = 401.7 \pm 0.6 \text{ kJ mol}^{-1}$  and  $\Delta_f H^\circ_{298}(\text{CH}_2\text{OH}) = -17.26 \pm 0.85 \text{ kJ mol}^{-1}$ .

(lj) An *ab initio* study for several species at the MP4/6-31+G(2df,p) level of theory, utilizing geometries optimized at the MP2/6-31G(d,p) level and thermal corrections derived from harmonic frequencies at the HF/6-31G level. For  $\text{CH}_2\text{OH}$ , three reactions have been studied: the isogyric reaction  $\text{CH}_2\text{OH} + 3\text{H} \rightarrow \text{C} + \text{O} + 3\text{H}_2$ , the C–O bond hydrogenation  $\text{CH}_2\text{OH} + \text{H}_2 \rightarrow \text{CH}_3 + \text{H}_2\text{O}$ , and the hydrogen exchange process  $\text{CH}_2\text{OH} + \text{CH}_4 \rightarrow \text{CH}_3\text{OH} + \text{CH}_3$ . The resulting 298.15 K enthalpies of formation for  $\text{CH}_2\text{OH}$  are  $-21.9$ ,  $-15.0$ , and  $-19.7 \text{ kJ mol}^{-1}$ , respectively. The authors find that the isogyric reaction tends to systematically underestimate the enthalpy of formation by  $\sim 6 \text{ kJ mol}^{-1}$ . The value listed in the table is an average of their results from the bond hydrogenation and hydrogen exchange reactions. At the MP4/6-31+G(2df,p) level the authors note for these two types of reactions an overall agreement of the order of  $6 \text{ kJ mol}^{-1}$  ( $1.5 \text{ kcal mol}^{-1}$ ).

(lk) The bond dissociation energy of  $D_0(\text{H}-\text{CH}_2\text{OH}) = 390.7 \text{ kJ mol}^{-1}$  computed at the MP4-SAC/6-311G\*\* level of theory using HF/6-31G geometries for  $\text{CH}_2\text{OH}$ . At the same level of theory but using MP2/6-31G geometries,  $D_0(\text{H}-\text{CH}_2\text{OH}) = 393.6 \text{ kJ mol}^{-1}$  was obtained. The authors note that HF geometries lead to lower electronic energies at the MP4/6-311G\*\* level than the MP2 geometries and hence favor the former. The favored bond dissociation energy, when used with auxiliary thermochemical data listed in (1a) above, leads to  $\Delta_f H^\circ_{298}(\text{CH}_2\text{OH}) = -21.8 \text{ kJ mol}^{-1}$ . Choosing instead the bond dissociation energy obtained from geometries optimized at the MP2 level would have led to  $\Delta_f H^\circ_{298}(\text{CH}_2\text{OH}) = -18.9 \text{ kJ mol}^{-1}$ .

(ll) Modified coupled-pair functional (MCPF) method with a large basis set. The C–H bond dissociation energy in  $\text{CH}_3\text{OH}$  was calculated to be  $D_0(\text{CH}_3\text{O}-\text{H}) = 94.2 \text{ kcal mol}^{-1} = 394.1 \text{ kJ mol}^{-1}$ . Based on previous experiences, the authors have added  $2 \text{ kcal mol}^{-1}$  to the computed C–H bond energy resulting in  $96.2 \pm 2 \text{ kcal mol}^{-1} = 402.5 \pm 8.4 \text{ kJ mol}^{-1}$ . Using the auxiliary thermochemical values listed in (1a) above, one obtains the bond dissociation

energy of methanol of  $409.0 \pm 8.4 \text{ kJ mol}^{-1}$  at 298.15 K, and hence  $\Delta_f H^\circ_{298}(\text{CH}_2\text{OH}) = -10.0 \pm 8.4 \text{ kJ mol}^{-1}$ .

(lm) MP4 and PMP4 *ab initio* calculations. Three basis sets were used: 6-311+G(d,p), 6-31+G(2df,p), and TZ(2df,p) on geometries optimized at the MP2/6-31G(d,p) level. The study includes estimates for post-MP4 corrections using the PMP-SAC4 method of Gordon and Truhlar<sup>50</sup> and the theoretical fourth-order invariant quantity of Feenberg.<sup>51</sup> The authors utilized the C–O bond hydrogenation  $\text{CH}_2\text{OH} + \text{H}_2 \rightarrow \text{CH}_3 + \text{H}_2\text{O}$  and the hydrogen exchange process  $\text{CH}_2\text{OH} + \text{CH}_4 \rightarrow \text{CH}_3\text{OH} + \text{CH}_3$  to propose  $\Delta_f H^\circ_{298}(\text{CH}_2\text{OH}) = -15.6 \pm 1.5 \text{ kJ mol}^{-1}$ . The authors recommend the quoted value, but do not detail its exact genesis. However, the recommended value appears to be an average of the various values (ranging between  $-14.25$  and  $-16.70 \text{ kJ mol}^{-1}$ ) obtained for the two reactions after inclusion of the post-MP4 corrections using the Feenberg method. In addition, the enthalpies of formation of  $\text{CH}_2\text{OH}$  resulting from calculations on the hydrogenation reaction appear systematically lower by  $1.4$ – $2.6 \text{ kJ mol}^{-1}$  than those obtained from the hydrogen exchange reaction. In view of this, the uncertainty given by the authors has been multiplied by a factor of 2 to bring it closer to the desired 95% confidence limit. In their computations, the authors used several sources for auxiliary enthalpies of formation<sup>23,52,43</sup> and thermal corrections.<sup>43,53,54</sup> While the authors do not give explicitly the enthalpy increments that were used to convert the values to 298.15 K, it was pointed out<sup>18</sup> that the 298.15 K thermal correction for  $\text{CH}_2\text{OH}$  derived<sup>53</sup> using harmonic frequencies for the torsion and  $\text{CH}_2$ -wag modes is too high. If, instead, the currently adopted enthalpy increment of Johnson and Hudgens<sup>16</sup> is used [see (1p) and (2c) below], a 298.15 K value for the enthalpy of formation of  $\text{CH}_2\text{OH}$  that is lower by  $\sim 2 \text{ kJ mol}^{-1}$  is obtained from the computed total energies.

(ln) The isodesmic reaction  $\text{CH}_3\text{OH} + \text{CH}_3 \rightarrow \text{CH}_2\text{OH} + \text{CH}_4$  studied using *ab initio* calculations at the HF, MP2 (cc-pVTZ and cc-pVQZ basis sets) and at the CCSD(T)/cc-pVTZ level. From these calculations,  $-37.7 \pm 0.8 \text{ kJ mol}^{-1}$  was obtained for the reaction enthalpy without the inclusion of the zero-point energy. With fundamental vibrational frequencies taken from the literature,<sup>45,55–58</sup> a zero point correction of  $+1.55 \text{ kJ mol}^{-1}$  to the reaction enthalpy was estimated. Using the computed reaction enthalpy, the zero-point energy and the experimental C–H bond dissociation energy in  $\text{CH}_4$ , a C–H bond dissociation energy in  $\text{CH}_3\text{OH}$  of  $D_0(\text{H}-\text{CH}_2\text{OH}) = 397.4 \pm 3.3 \text{ kJ mol}^{-1}$  was obtained. This value, together with auxiliary thermochemical values,<sup>59,60</sup> leads to an 0 K enthalpy of formation of  $-8.4 \pm 13.3 \text{ kJ mol}^{-1}$  for  $\text{CH}_2\text{OH}$ . Treating the rotation about the C–O bond as a hindered rotation results in a  $[H^\circ(298.15 \text{ K}) - H^\circ(0 \text{ K})]$  value of  $11.21 \text{ kJ mol}^{-1}$  for  $\text{CH}_2\text{OH}$ , which is very similar to that computed<sup>6</sup> by treating all modes as vibrations. Using this  $[H^\circ(298.15 \text{ K}) - H^\circ(0 \text{ K})]$  for  $\text{CH}_2\text{OH}$  results in an enthalpy of formation of  $-15.3 \pm 3.5 \text{ kJ mol}^{-1}$  at 298.15 K.

(lo) BAC-MP4 *ab initio* calculations. The originally quoted



uncertainty of  $\pm 4.6 \text{ kJ mol}^{-1}$  was multiplied by factor of 2 to bring it closer to the desired 95% confidence limit.

(1p) A combined spectroscopic and computational study. In the spectroscopic portion of their study, the authors show conclusively that the  $\nu_8$  torsion and  $\nu_9$   $\text{CH}_2$ -wag are strongly coupled anharmonic motions and should be treated together. By solving a potential energy surface for these two modes calculated at the MP2/6-311G(2df,2p) level of theory, the authors obtain the corresponding vibrational levels, which are then verified by comparison to the experimentally observed transitions. The computed levels of this potential are subsequently used to obtain the partition function of  $\text{CH}_2\text{OH}$  by computing the thermochemical contributions of these two modes through a direct count, and hence providing the currently best available treatment of heat capacity, entropy, and enthalpy increments for this species, which are the values adopted in the present evaluation [see (2c) below].

The theoretical value for the enthalpy of formation of  $\text{CH}_2\text{OH}$  was obtained by studying the isodesmic reaction  $\text{CH}_2\text{OH} + \text{CH}_4 \rightarrow \text{CH}_3\text{OH} + \text{CH}_3$  using CBS-QCI/APNO calculations. The *ab initio* reaction enthalpy was obtained from the computed total energies for the reactants and products. Zero-point energies were corrected for the nonharmonic character of torsion and inversion modes by using experimental data as discussed above. With the corrected reaction enthalpy and auxiliary enthalpies of formation<sup>43,49</sup> for the remaining species participating in the reaction, the 0 K enthalpy of formation of  $\Delta_f H^\circ_0(\text{CH}_2\text{OH}) = -12.1 \pm 1.3 \text{ kJ mol}^{-1}$  is obtained. Finally, a correction of  $-6.3 \text{ kJ mol}^{-1}$  (based on their  $[H^\circ(298.15 \text{ K}) - H^\circ(0 \text{ K})](\text{CH}_2\text{OH}) = -11.781 \text{ kJ mol}^{-1}$ ) is applied to obtain  $\Delta_f H^\circ_{298}(\text{CH}_2\text{OH}) = -18.4 \pm 1.3 \text{ kJ mol}^{-1}$ . The quoted uncertainty corresponds to one standard deviation (as explicitly stated by the authors), and has been multiplied by a factor of two to bring it closer to the 95% confidence limit. In addition, the authors review the available experimental data and derive a recommended experimental value [see (1z) below]. (1q) CBS-Q value. The value listed in the table is converted from  $3.8 \text{ kcal mol}^{-1}$ . The reported average absolute deviation of  $1.57 \text{ kcal mol}^{-1}$  was multiplied by 2 to bring it closer to the desired 95% confidence limit. The equivalent CBS-q and CBS-4 enthalpies of formation are  $-9.2 \pm 18 \text{ kJ mol}^{-1}$  ( $-2.2 \text{ kcal mol}^{-1}$ ) and  $-14.2 \pm 26 \text{ kJ mol}^{-1}$  ( $-3.4 \text{ kcal mol}^{-1}$ ), where the uncertainties have been obtained in an analogous way.

(1r) G3 *ab initio* calculation. The value listed in the table is converted from  $-3.9 \text{ kcal mol}^{-1}$ . The uncertainty quoted in the table corresponds approximately to 95% confidence limits, based on twice the average absolute deviation of  $0.94 \text{ kcal mol}^{-1}$  for the enthalpies in the G2/97 test set, which roughly corresponds to 1 s.d. deviation. At the G3(MP2) level of theory<sup>61</sup>  $\Delta_f H^\circ_{298}(\text{CH}_2\text{OH}) = -15.1 \pm 9.9 \text{ kJ mol}^{-1}$  ( $-3.6 \text{ kcal mol}^{-1}$ ), where the quoted uncertainty has been derived in a similar fashion as for the G3 value. At the G2 level of theory<sup>62</sup>  $\Delta_f H^\circ_{298}(\text{CH}_2\text{OH}) = -15.5 \pm 13.1 \text{ kJ mol}^{-1}$  ( $-3.7 \text{ kcal mol}^{-1}$ ).

(1s) W1 *ab initio* computation. The uncertainty quoted in the

table corresponds approximately to 95% confidence limits based on twice the average absolute deviation of  $0.37 \text{ kcal mol}^{-1}$  for the W1 test set, which corresponds roughly to 1 s.d.

(1t) Bond dissociation energies for monosubstituted methyl radicals calculated at a variety of levels including CBS-RAD, G3(MP2)-RAD, and W1'. The values for  $D_0(\text{H}-\text{CH}_2\text{OH})$  obtained with W1', G3(MP2)-RAD and CBS-RAD, the three methods which were generally close to the experimental values, were 397.0, 394.8, and 398.6  $\text{kJ mol}^{-1}$ , respectively. From these, one obtains an average  $D_0(\text{H}-\text{CH}_2\text{OH}) = 396.8 \text{ kJ mol}^{-1}$  which, together with auxiliary thermochemical data detailed in (1a), leads to  $\Delta_f H^\circ_0(\text{CH}_2\text{OH}) = -9.5 \text{ kJ mol}^{-1}$  and  $\Delta_f H^\circ_{298}(\text{CH}_2\text{OH}) = -15.7 \text{ kJ mol}^{-1}$ . The authors state that the maximum absolute deviation for W1', G3(MP2)-RAD and CBS-RAD were 3.1, 2.4, and 2.9  $\text{kJ mol}^{-1}$ , respectively. These suggest an associated uncertainty of  $\pm 3 \text{ kJ mol}^{-1}$ .

(1u) G3(MP2)//B3LYP *ab initio* calculations for 32 selected free radicals. The uncertainty given in the table corresponds approximately to 95% confidence limits based on twice the quoted average absolute deviation of  $3.9 \text{ kJ mol}^{-1}$  for the calculated set of radicals, which corresponds roughly to 1 s.d. Note that the average absolute deviation for all enthalpies in the G2/97 test set using the same method is very slightly larger:<sup>63</sup>  $4.7 \text{ kJ mol}^{-1}$  [see also (1t) above].

(1v) CCSD(T)/aug-cc-pVnZ ( $n = T, Q, 5$ ) *ab initio* calculations extrapolated to complete basis set and corrected for core-valence and relativistic effects on the reaction  $\text{CH}_2\text{OH} \rightarrow \text{CH}_2\text{O} + \text{H}$ , resulting in  $\Delta_r H^\circ(0 \text{ K}) = 121.7 \pm 0.2 \text{ kJ/mol}$ . Zero-point energies of  $\text{CH}_2\text{OH}$  ( $94.8 \pm 0.1 \text{ kJ/mol}$ ) and  $\text{CH}_2\text{O}$  ( $69.3 \pm 0.1 \text{ kJ/mol}$ ) and the enthalpy increment  $[H^\circ(298.15 \text{ K}) - H^\circ(0 \text{ K})](\text{CH}_2\text{OH}) = -11.674 \text{ kJ mol}^{-1}$  were calculated using the highly anharmonic potential surface derived by Marenich and Boggs.<sup>64</sup>  $\Delta_f H^\circ_0(\text{CH}_2\text{O}) = -104.86 \pm 0.50 \text{ kJ/mol}$  ( $-108.7 \pm 0.5 \text{ kJ/mol}$  at 298.15 K) was taken from Gurvich *et al.*<sup>24</sup> Combining these data gave  $\Delta_f H^\circ_0(\text{CH}_2\text{OH}) = -10.5 \pm 0.7 \text{ kJ/mol}$  and  $\Delta_f H^\circ_{298}(\text{CH}_2\text{OH}) = -16.9 \pm 0.7 \text{ kJ/mol}$ .

(1w) Recommended value from extensive evaluation of data (mainly kinetic determinations) published until 1981. The recommended value is based on two previous reviews.

(1x) Extensive compilation of thermodynamic data. The selected value of  $\Delta_f H^\circ_{298}(\text{CH}_2\text{OH}) = -20 \pm 10 \text{ kJ mol}^{-1}$  is a weighted average of seven determinations (three kinetic and four appearance potential measurements) ranging from  $-70 \pm 50 \text{ kJ mol}^{-1}$  up to  $-1 \pm 35 \text{ kJ mol}^{-1}$ .

(1y) An evaluation of literature data. From the proton affinity of  $\text{CH}_2\text{O}$ , calculated by Smith and Radom<sup>65</sup> at the G2 level of theory as  $711.8 \text{ kJ mol}^{-1}$ , an enthalpy of formation of  $\Delta_f H^\circ_{298}(\text{CH}_2\text{OH}^+) = 709.9 \text{ kJ mol}^{-1}$  was derived. Furthermore, from the reaction enthalpy<sup>35</sup> of  $\Delta_r H^\circ_{298} = 0.42 \text{ kJ mol}^{-1}$  for the proton-exchange reaction  $\text{CH}_2\text{O} + \text{HCNH}^+ \rightarrow \text{CH}_2\text{OH}^+ + \text{HCN}$ ,  $\Delta_f H^\circ_{298}(\text{CH}_2\text{OH}^+) = 706.3 \text{ kJ mol}^{-1}$  was obtained. The average of these two values,  $\Delta_f H^\circ_{298}(\text{CH}_2\text{OH}^+) = 707.9 \text{ kJ mol}^{-1}$ , together with integrated heat capacities<sup>6,66</sup> and a selected ionization energy

of  $E_i(\text{CH}_2\text{OH}) = 7.56 \text{ eV}$  was then used to derive  $\Delta_f H^\circ_{298}(\text{CH}_2\text{OH}) = -20.4 \text{ kJ mol}^{-1}$ .

(1z) Critical data evaluation of R–H bond dissociation energies based on three methods: kinetic determinations, positive ion cycle determinations from photoelectron/photoionization measurements, and negative ion cycle determinations from photoelectron measurements of negative ions combined with gas phase acidities. The recommended value is based on the positive ion cycle, derived using  $E_{\text{ap},0}(\text{CH}_2\text{OH}^+/\text{CH}_3\text{OH}) = 11.649 \pm 0.003 \text{ eV}$  and a corrected value  $E_{i,\text{ad}}(\text{CH}_2\text{OH}) = 7.553 \pm 0.006 \text{ eV}$  from Ruscic and Berkowitz,<sup>7,48</sup> together with auxiliary thermochemical values from Gurvich *et al.*<sup>24</sup> The amended value of  $E_{i,\text{ad}}(\text{CH}_2\text{OH})$  corrects the inadvertent conversion error from wavelength to energy that occurred previously.<sup>48</sup> The conversions to 298.15 K of the C–H bond dissociation energy in methanol and enthalpy of formation of  $\text{CH}_2\text{OH}$  make use of the enthalpy increment for  $\text{CH}_2\text{OH}$  that is based on a hindered rotor approach.<sup>7</sup>

(1aa) Combined spectroscopic and computational study described in more detail above [see (1p)]. From their studies, the authors provide a sophisticated treatment of the partition function for  $\text{CH}_2\text{OH}$ . They also compute  $\Delta_f H^\circ(\text{CH}_2\text{OH})$  at the CBS-QCI/APNO level of theory. Finally, the authors review the available experimental data and derive a recommended experimental value for the enthalpy of formation of  $\text{CH}_2\text{OH}$ . The recommended values,  $\Delta_f H^\circ_{298}(\text{CH}_2\text{OH}) = -17.8 \pm 1.3 \text{ kJ mol}^{-1}$  and  $\Delta_f H^\circ_0(\text{CH}_2\text{OH}) = -11.5 \pm 1.3 \text{ kJ mol}^{-1}$ , are weighted averages of values derived from the positive ion cycle, kinetic equilibrium studies, and shock tube results. (i) The appearance energy  $E_{\text{ap},0}(\text{CH}_2\text{OH}^+/\text{CH}_3\text{OH}) = 11.650 \pm 0.019 \text{ eV}$  was obtained as the average of available literature values.<sup>6,7,36</sup> From this,  $\Delta_f H^\circ_0(\text{CH}_2\text{OH}^+) = 718.1 \pm 1.8 \text{ kJ mol}^{-1}$  was derived using auxiliary enthalpies of formation<sup>43,49</sup> and converted to  $\Delta_f H^\circ_{298}(\text{CH}_2\text{OH}^+) = 716.6 \pm 1.8 \text{ kJ mol}^{-1}$  by making use of their computed enthalpy increment for  $\text{CH}_2\text{OH}$ . Similarly, an adiabatic ionization energy of  $E_{i,\text{ad}}(\text{CH}_2\text{OH}) = 7.562 \pm 0.04 \text{ eV}$  was derived by averaging published ionization energies<sup>1,3,25,67</sup> and used to obtain  $\Delta_f H^\circ_0(\text{CH}_2\text{OH}) = -11.6 \pm 1.9 \text{ kJ mol}^{-1}$  or  $\Delta_f H^\circ_{298}(\text{CH}_2\text{OH}) = -17.9 \pm 1.9 \text{ kJ mol}^{-1}$ . (ii) Results of previous kinetic equilibrium studies<sup>4,5,8,44</sup> were reevaluated using their entropy and heat capacity values for  $\text{CH}_2\text{OH}$  [including  $S^\circ_{298}(\text{CH}_2\text{OH}) = 244.170 \text{ J mol}^{-1} \text{ K}^{-1}$ ] to obtain the third-law enthalpy of formation of  $\Delta_f H^\circ_{298}(\text{CH}_2\text{OH}) = -17.6 \pm 1.9 \text{ kJ mol}^{-1}$ . (iii) In a shock tube study by Tsang,<sup>68</sup>  $\Delta_f H^\circ_{298}(\text{CH}_2\text{OH}) = -17.6 \pm 8 \text{ kJ mol}^{-1}$  was estimated by comparing the relative stability of  $\text{CH}_3\text{OH}$  with  $\text{CH}_4$  and referencing these data to the  $\text{CH}_3\text{–H}$  bond strength. The stated uncertainty has an intended meaning of 1 s.d.

(1bb) Critical data evaluation for selected free radicals based on kinetic measurements. The recommended value is based on the results of Seetula and Gutman<sup>4</sup> and of Dóbe *et al.*<sup>5</sup>

(1cc) Critical data evaluation. Considering a wide range of literature data, the enthalpy of formation for  $\text{CH}_2\text{OH}^+$ ,  $\Delta_f H^\circ_{298}(\text{CH}_2\text{OH}^+) = 708.6 \pm 0.9 \text{ kJ mol}^{-1}$ , and the “298.15 K ionization energy” for  $\text{CH}_2\text{OH}$ , of  $727.4 \pm 1.0 \text{ kJ mol}^{-1}$

was selected. Combining these quantities, an enthalpy of formation of  $\Delta_f H^\circ_{298}(\text{CH}_2\text{OH}) = -18.8 \pm 1.3 \text{ kJ mol}^{-1}$  is derived.

(1dd) The compilation lists theoretical results at various levels of theory, but also makes a reference to one experimental benchmark. The quoted experimental benchmark value is from Johnson and Hudgens<sup>16</sup> [see (1aa) above].

(1ee) Critical evaluation of atmospherically relevant kinetic rates. Their table of enthalpy data lists the value reported by Johnson and Hudgens<sup>16</sup> [see (1aa) above].

(1ff) Thermodynamic data compilation. The preferred value is that reported by Johnson and Hudgens<sup>16</sup> [see (1aa) above].

(1gg) Thermodynamic database for combustion. The preferred value is that reported by Johnson and Hudgens<sup>16</sup> [see (1aa) above].

(1hh) Critical evaluation of atmospherically relevant kinetic data. The origin of the value is unclear. The authors quote Johnson and Hudgens<sup>16</sup> [see (1aa) above], who recommend  $-17.8 \pm 1.3 \text{ kJ/mol}$ .

(1ii) An unevaluated tabulation of available values from other sources. The source for the listed value is quoted as Tsang.<sup>68</sup>

### Preferred Value of the Enthalpy of Formation

$$\Delta_f H^\circ(298.15 \text{ K}) = -17.0 \pm 0.7 \text{ kJ mol}^{-1}$$

$$\Delta_f H^\circ(0 \text{ K}) = -10.7 \pm 0.7 \text{ kJ mol}^{-1}$$

In the enthalpies of formation reported before 1993, there was considerable difference between the values derived from photoionization mass spectrometric determinations and from kinetic equilibrium studies; the former values being significantly lower than the latter ones. However, the results of recent determinations converged, particularly after the kinetic measurements made use of a more elaborately estimated entropy of  $\text{CH}_2\text{OH}$  and after improved values that are needed to close the positive ion cycle became available. Thus, in the identification of the best enthalpy of formation value, only recent determinations were considered.

The weighted average of the two most recent experimental determinations, the kinetic equilibrium study by Dóbe *et al.*,<sup>8</sup> and the PIMS-PIC value of Litorja and Ruscic,<sup>9</sup> results in  $\Delta_f H^\circ_{298}(\text{CH}_2\text{OH}) = -17.1 \pm 4.2 \text{ kJ mol}^{-1}$ , where the relatively large uncertainty reflects a 95% confidence limit resulting from the consideration of only two determinations. However, if the weighted average also includes the highly accurate *ab initio* calculation of Marenich and Boggs,<sup>22</sup> the value remains essentially unchanged, but the uncertainty becomes considerably lower,  $\Delta_f H^\circ_{298}(\text{CH}_2\text{OH}) = -17.0 \pm 0.7 \text{ kJ mol}^{-1}$ .

The preferred value is the weighted average of the results of the kinetic equilibrium study by Dóbe *et al.*,<sup>8</sup> the PIMS-PIC value of Litorja and Ruscic<sup>9</sup> and the *ab initio* calculations of Marenich and Boggs.<sup>22</sup> This preferred value is in good agreement with the weighted average of all experimental determinations ( $-16.6 \pm 1.9 \text{ kJ mol}^{-1}$ ), and agrees par-

ticularly well with the weighted average of experimental determinations when the two kinetic measurements<sup>4,5</sup> that employed less sophisticated entropy values for CH<sub>2</sub>OH are either excluded ( $-17.3 \pm 0.9 \text{ kJ mol}^{-1}$ ) or lowered ( $-17.0 \pm 1.0 \text{ kJ mol}^{-1}$ ) as suggested in the comments [see (1d) and (1e) above]. The preferred value also agrees quite well with the weighted average of the listed computational results ( $-16.9 \pm 0.7 \text{ kJ mol}^{-1}$ , or, even when the most recent computational result of Marenich and Boggs<sup>22</sup>—which carries considerable weight in the average—is excluded,  $-17.0 \pm 1.4 \text{ kJ/mol}$ ).

The preferred value corresponds to  $D_{298}(\text{H}-\text{CH}_2\text{OH}) = 402.0 \pm 0.9 \text{ kJ mol}^{-1}$  ( $395.5 \pm 0.9 \text{ kJ mol}^{-1}$  at 0 K), which produces the listed enthalpy when used together with auxiliary thermochemical values from Gurvich *et al.*<sup>24</sup>

$\Delta_f H^\circ_{298}(\text{CH}_3\text{OH}) = -201.0 \pm 0.60 \text{ kJ mol}^{-1}$ ,  $[H^\circ(298.15 \text{ K}) - H^\circ(0 \text{ K})](\text{CH}_3\text{OH}) = 11.441 \text{ kJ mol}^{-1}$  (note that—without giving uncertainties—*TRC Thermochemical Tables*<sup>49</sup> list very similar values of  $\Delta_f H^\circ_{298}(\text{CH}_3\text{OH}) = -200.94 \text{ kJ mol}^{-1}$  and  $11.440 \text{ kJ mol}^{-1}$  for the enthalpy increment), and CODATA<sup>37</sup> recommended values  $\Delta_f H^\circ_{298}(\text{H}) = 217.998 \pm 0.006 \text{ kJ mol}^{-1}$ ,  $[H^\circ(298.15 \text{ K}) - H^\circ(0 \text{ K})](\text{H}) = 6.197 \pm 0.001 \text{ kJ mol}^{-1}$ ,  $[H^\circ(298.15 \text{ K}) - H^\circ(0 \text{ K})](\text{C, graphite}) = 1.050 \pm 0.020 \text{ kJ mol}^{-1}$ ,  $[H^\circ(298.15 \text{ K}) - H^\circ(0 \text{ K})](\text{C}) = 6.536 \pm 0.001 \text{ kJ mol}^{-1}$ ,  $[H^\circ(298.15 \text{ K}) - H^\circ(0 \text{ K})](\text{H}_2) = 8.468 \pm 0.001 \text{ kJ mol}^{-1}$ , and  $[H^\circ(298.15 \text{ K}) - H^\circ(0 \text{ K})](\text{O}_2) = 8.680 \pm 0.002 \text{ kJ mol}^{-1}$ , together with  $[H^\circ(298.15 \text{ K}) - H^\circ(0 \text{ K})](\text{CH}_2\text{OH}) = -11.781 \text{ kJ mol}^{-1}$  as listed below.

Geometry (distance in Å, angles in degrees)<sup>(2a)</sup>

Z matrix						Cartesian coordinates				
						x	y	z		
C					C	0.000 000	0.014 784	-0.724 810		
O	1	1.3622			O	0.000 000	-0.065 606	0.635 046		
H	2	0.9576	1	109.19	H	0.000 000	0.818 601	1.002 657		
H	1	1.0742	2	115.20	3	180.00	H	0.000 000	-0.928 470	-1.238 751
H	1	1.0770	2	120.30	3	0.00	H	0.000 000	0.975 054	-1.212 358

Moments of Inertia in the Electronic Ground State<sup>(2a)</sup>

$$I_A = 4.274 \times 10^{-47} \text{ kg m}^2$$

$$I_B = 27.890 \times 10^{-47} \text{ kg m}^2$$

$$I_C = 32.164 \times 10^{-47} \text{ kg m}^2$$

Vibrational wave numbers in the electronic ground state  $\nu_i(\text{cm}^{-1})$ <sup>(2b)</sup>

3650 ( <i>a'</i> )	3169 ( <i>a'</i> )	3071 ( <i>a'</i> )
1459 ( <i>a'</i> )	1334 ( <i>a'</i> )	1176 ( <i>a'</i> )
1048 ( <i>a'</i> )	420 ( <i>a''</i> )	234 ( <i>a''</i> )

Heat Capacity  $C_p^\circ$ , Entropy  $S^\circ$ , and Enthalpy Increment  $[H^\circ(T) - H^\circ(0 \text{ K})]$ <sup>(2c),(2d),(2e)</sup>

T/K	$C_p^\circ(T)$ ( $\text{J K}^{-1} \text{ mol}^{-1}$ )	$S^\circ(T)$ ( $\text{J K}^{-1} \text{ mol}^{-1}$ )	$[H^\circ(T) - H^\circ(0 \text{ K})]$ ( $\text{kJ mol}^{-1}$ )
100	37.074	199.004	3.415
200	42.183	226.401	7.396
250	44.658	236.074	9.566
298.15	47.401	244.170	11.781
300	47.512	244.464	11.869
350	50.591	252.018	14.321
400	53.681	258.977	16.928
500	59.356	271.582	22.587
600	64.113	282.839	28.768
800	71.474	302.348	42.329
1000	77.058	318.924	57.241
1200	81.458	333.379	73.110
1500	86.375	352.118	98.329
2000	91.464	377.739	142.917

## 7-Constant NASA Polynomial

CH2OH RADICAL	JUN03 C	1.H	3.0	1.	0.G	200.000	6000.000	31.03392	1
0.50931437E+01	0.59476126E-02	-0.20649746E-05	0.32300817E-09	-0.18812590E-13	2				
-0.40340964E+04	-0.18469149E+01	0.44783436E+01	-0.13507031E-02	0.27848498E-04	3				
-0.36486906E-07	0.14790745E-10	-0.35007289E+04	0.33091350E+01	-0.20446277E+04	4				

## 9-Constant NASA Polynomial

CH2OH RADICAL	NASA/Johnson,1996 Mod. IUPAC Task Group on Selected Radicals										
2 g11/00 C	1.00H	3.000	1.00	0.00	0.00s0	31.03392	-17000.000				
200.000	1000.000	7	-2.0	-1.0	0.0	1.0	2.0	3.0	4.0	0.0	11781.000
-1.560076238E+05	2.685446279E+03	-1.342022420E+01	5.757139470E-02	-7.284449990E-05							
4.836648860E-08	-1.293492601E-11	0.000000000E+00	-1.587198632E+04	9.963033700E+01							
1000.000	6000.000	7	-2.0	-1.0	0.0	1.0	2.0	3.0	4.0	0.0	11781.000
2.250349506E+06	-8.173186060E+03	1.599639179E+01	-8.704133720E-04	6.069183950E-08							
4.408349460E-12	-5.702309500E-16	0.000000000E+00	4.654935208E+04	-7.835158450E+01							

### Comments on Molecular Data, Heat Capacity, Entropy, and Enthalpy Increment

(2a) The ground potential energy surface of CH<sub>2</sub>OH has four C<sub>1</sub> equivalent minima.<sup>16,64,69</sup> Interconversion between these minima occur along strongly coupled anharmonic motions: internal rotation around the C–O bond ( $\nu_8$  torsion) and CH<sub>2</sub>-wag (i.e., CH<sub>2</sub> inversion,  $\nu_9$ ). Due to the extremely low barrier along the inversion pathway, the motion can be considered as a large amplitude vibration centered around a C<sub>s</sub> structure, which connects two mirror-image shallow C<sub>1</sub> minima. The structural data (Z-matrix and Cartesian coordinates) and principal moments of inertia are for such a planar (C<sub>s</sub>) structure, and are the results of CCSD(T)/aug-cc-pVnZ ( $n=T,Q,5$ ) *ab initio* calculations extrapolated to complete basis set.<sup>64</sup> Jacox<sup>70,71</sup> has made a similar selection, and consequently lists C<sub>s</sub> as the experimentally observed symmetry of CH<sub>2</sub>OH.

(2b) The vibrational wavenumbers are based primarily on experimentally observed fundamentals.<sup>70,71,57,16</sup> The  $\nu_2$  and  $\nu_3$  modes (given in italics) are not known experimentally, and were derived from MP2/6-311G(2df, 2p) *ab initio* results of Johnson and Hudgens<sup>16</sup> (scaled by 0.94). Marenich and Boggs<sup>64</sup> obtain similar values of 3208 and 3060 cm<sup>-1</sup> for these two modes at the CCSD(T)/aug-cc-pVQZ level by anharmonic analysis by the perturbation theory calculations for the C<sub>1</sub> structure. Note that the analysis of the vibrational hot bands in the REMPI spectra by Johnson and Hudgens<sup>16</sup> shows that the  $\nu_8$  torsion mode and  $\nu_9$  CH<sub>2</sub>-wag mode (the last two values listed above) are strongly coupled and governed by nonharmonic potential energy functions. This is fully corroborated by subsequent theoretical treatments, such as those by Johnson and Hudgens<sup>16</sup> and Marenich and Boggs.<sup>64</sup>

(2c) The heat capacities, enthalpy increments, and entropies are those reported by Johnson and Hudgens.<sup>16</sup> The adopted functions are based on computing the thermochemical contributions of the coupled  $\nu_8$  torsion and  $\nu_9$  CH<sub>2</sub>-wag through a direct count of vibrational levels obtained by solving the relevant potential obtained at the MP2 level of theory and comparing to observed spectroscopic transitions [see (1p) above]. Marenich and Boggs<sup>22,64</sup> have recently obtained very similar results by a variational study of nuclear dynamics of

CH<sub>2</sub>OH using a potential energy surface obtained at the CCSD(T) level of theory. The thermochemical functions given above differ significantly from those obtained by treating the internal OH-rotor ( $\nu_8$  torsion) as a free rotor,<sup>42</sup> a pseudovibration,<sup>6</sup> or even a hindered rotor.<sup>7</sup>

(2d) The nine-constants NASA polynomial is based on heat capacities, enthalpy increments and entropies reported by Johnson and Hudgens<sup>16</sup> and suitably extended to higher temperatures.<sup>72</sup> The seven-constants NASA polynomial has been obtained by fitting the values given by Johnson and Hudgens<sup>16</sup> and listed in the table above, together with values obtained from the 9-constants NASA polynomial for temperatures in the range 2000–6000 K.

(2e) The standard heat capacity, entropy, and enthalpy increment values reported in the compilation of Gurvich *et al.*<sup>24</sup> are  $C_p^\circ(298.15\text{ K}) = 46.479\text{ J K}^{-1}\text{ mol}^{-1}$ ,  $S^\circ(298.15\text{ K}) = 245.747\text{ J K}^{-1}\text{ mol}^{-1}$ ,  $H^\circ(298.15\text{ K}) - H^\circ(0\text{ K}) = 11.196\text{ kJ mol}^{-1}$ , in the *Thermochemical Database for Combustion*<sup>32</sup> are  $C_p^\circ(298.15\text{ K}) = 48.369\text{ J K}^{-1}\text{ mol}^{-1}$ ,  $S^\circ(298.15\text{ K}) = 243.919\text{ J K}^{-1}\text{ mol}^{-1}$ , and those obtained from G3MP2B3 computations<sup>21</sup> are  $C_p^\circ(298.15\text{ K}) = 46.36\text{ J K}^{-1}\text{ mol}^{-1}$ ,  $S^\circ(298.15\text{ K}) = 239.83\text{ J K}^{-1}\text{ mol}^{-1}$ ,  $H^\circ(298.15\text{ K}) - H^\circ(0\text{ K}) = 11.18\text{ kJ mol}^{-1}$ .

### References

- J. M. Dyke, A. E. Ellis, N. Jonathan, N. Keddar, and A. Morris, *Chem. Phys. Lett.* **111**, 207 (1984); see also: J. M. Dyke, *J. Chem. Soc. Faraday Trans. II* **83**, 69 (1987).
- J. L. Holmes and F. P. Lossing, *Int. J. Mass Spectrom.* **58**, 113 (1984).
- B. Ruscic and J. Berkowitz, *J. Chem. Phys.* **95**, 4033 (1991).
- J. A. Seetula and D. Gutman, *J. Phys. Chem.* **96**, 5401 (1992).
- S. Dóbe, M. Otting, F. Temps, H. Gg. Wagner, and H. Ziemer, *Ber. Bunsenges. Phys. Chem.* **97**, 877 (1993).
- J. C. Traeger and J. L. Holmes, *J. Phys. Chem.* **97**, 3453 (1993).
- B. Ruscic and J. Berkowitz, *J. Phys. Chem.* **97**, 11451 (1993).
- S. Dóbe, T. Bérces, T. Turányi, F. Márta, J. Grussdorf, F. Temps, and H. Gg. Wagner, *J. Phys. Chem.* **100**, 19864 (1996).
- M. Litorja and B. Ruscic, *J. Electron Spectrosc.* **97**, 131 (1998).
- M. Sana and G. Leroy, *J. Mol. Struct. (Theochem)* **226**, 307 (1991).
- L. Pardo, J. R. Banfelder, and R. Osman, *J. Am. Chem. Soc.* **114**, 2382 (1992).
- C. W. Bauschlicher, Jr., S. R. Langhoff, and S. P. Walch, *J. Chem. Phys.* **96**, 450 (1992).
- J. Espinoza-Garcia and F. J. Olivares del Valle, *J. Phys. Chem.* **97**, 3377 (1993).

- <sup>14</sup>C. W. Bauschlicher, Jr. and H. Partridge, *J. Phys. Chem.* **98**, 1826 (1994).
- <sup>15</sup>M. R. Zachariah, P. R. Westmoreland, D. R. Burgess, Jr., W. Tsang, and C. F. Melius, *J. Phys. Chem. A* **100**, 8737 (1996); see also D. R. F. Burgess, Jr., M. R. Zachariah, W. Tsang, and P. R. Westmoreland, *Prog. Energy Combust. Sci.* **21**, 453 (1995).
- <sup>16</sup>R. D. Johnson III and J. W. Hudgens, *J. Phys. Chem.* **100**, 19874 (1996).
- <sup>17</sup>L. A. Curtiss, K. Raghavachari, P. C. Redfern, and B. S. Stefanov, *J. Chem. Phys.* **108**, 692 (1998).
- <sup>18</sup>L. A. Curtiss, K. Raghavachari, P. C. Redfern, V. Rassolov, and J. A. Pople, *J. Chem. Phys.* **109**, 7764 (1998).
- <sup>19</sup>S. Parthiban and J. M. L. Martin, *J. Chem. Phys.* **114**, 6014 (2001).
- <sup>20</sup>D. J. Henry, C. J. Parkinson, P. M. Mayer, and L. Radom, *J. Phys. Chem. A* **105**, 6750 (2001).
- <sup>21</sup>R. Janoschek and M. J. Rossi, *Int. J. Chem. Kinet.* **34**, 550 (2002).
- <sup>22</sup>A. V. Marenich and J. E. Boggs (private communication); see also A. V. Marenich and J. E. Boggs, *J. Chem. Phys.* **119**, 3098 (2003), and Ref. 64.
- <sup>23</sup>D. F. McMillen and D. M. Golden, *Annu. Rev. Phys. Chem.* **33**, 493 (1982).
- <sup>24</sup>L. V. Gurvich, I. V. Veyts, and C. B. Alcock, *Thermodynamic Properties of Individual Substances*, 4th ed. (Hemisphere, New York, 1991), Vol. 2.
- <sup>25</sup>S.-C. Kuo, Z. Zhang, R. B. Klemm, J. F. Liebman, L. J. Stief, and F. L. Nesbitt, *J. Phys. Chem.* **98**, 4026 (1994).
- <sup>26</sup>J. Berkowitz, G. B. Ellison, and D. Gutman, *J. Phys. Chem.* **98**, 2744 (1994).
- <sup>27</sup>W. Tsang, *Heats of Formation of Organic Free Radicals by Kinetic Methods*, in *Energetics of Organic Free Radicals*, edited by J. A. M. Simoes, A. Greenberg, and J. F. Liebman, Structure, Energetics and Reactivity in Chemistry (SEARCH) Series (Chapman and Hall, London, 1996).
- <sup>28</sup>J. C. Traeger and B. M. Kompe, *Thermochemical Data for Free Radicals from Studies of Ions*, in *Energetics of Organic Free Radicals*, edited by J. A. M. Simoes, A. Greenberg, and J. F. Liebman, Structure, Energetics and Reactivity in Chemistry (SEARCH) Series (Chapman and Hall, London, 1996).
- <sup>29</sup>Computational Chemistry Comparison and Benchmark DataBase (CCCBDB), NIST (1999); see <http://srdata.nist.gov/cccbdb/>
- <sup>30</sup>R. Atkinson, D. L. Baulch, R. A. Cox, R. F. Hampson, Jr., J. A. Kerr, M. J. Rossi, and J. Troe, *J. Phys. Chem. Ref. Data* **29**, 167 (2000).
- <sup>31</sup>J. A. Kerr and D. W. Stocker, *Strengths of Chemical Bonds*, in *CRC Handbook of Chemistry and Physics*, edited by D. Lide, 82nd ed. (CRC Press, Boca Raton, FL, 2001–2002).
- <sup>32</sup>A. Burcat, TAE Report No.867, Technion, Haifa, 2001; see also <ftp://ftp.technion.ac.il/pub/supported/aetdd/thermodynamics>
- <sup>33</sup>S. P. Sander, R. R. Friedl, D. M. Golden, M. J. Kurylo, R. E. Huie, V. L. Orkin, G. K. Moortgat, A. R. Ravishankara, C. E. Kolb, M. J. Molina, and B. J. Finlayson-Pitts, JPL Publication 02-25, NASA and JPL, February 1, 2003.
- <sup>34</sup>H. Y. Afeefy, J. F. Liebman, and S. E. Stein, *Neutral Thermochemical Data*, in *NIST Chemistry WebBook*, NIST Standard Reference Database Number 69, edited by P. J. Linstrom and W. G. Mallard (NIST, Gaithersburg, MD, 2003) (<http://webbook.nist.gov>)
- <sup>35</sup>K. Tanaka, G. I. MacKay, and D. K. Bohne, *Can. J. Chem.* **56**, 193 (1978).
- <sup>36</sup>K. M. A. Refaey and W. A. Chupka, *J. Chem. Phys.* **48**, 5205 (1968).
- <sup>37</sup>J. D. Cox, D. D. Wagman, and V. A. Medvedev, *CODATA Key Values for Thermodynamics* (Hemisphere, New York, 1998); see also (<http://www.codata.org/codata/databases/key1.html>)
- <sup>38</sup>F. P. Lossing, *J. Am. Chem. Soc.* **99**, 7526 (1977).
- <sup>39</sup>F. P. Lossing, Y.-T. Lam, and A. Maccoll, *Can. J. Chem.* **59**, 2228 (1981).
- <sup>40</sup>J. B. Pedley and J. Rylance, *Sussex-NPL Computer Analyzed Thermochemical Data: Organic and Organometallic Compounds* (University of Sussex, Sussex, 1977).
- <sup>41</sup>E. Buckley and E. Whittle, *Trans. Faraday Soc.* **58**, 536 (1962).
- <sup>42</sup>W. Tsang, *J. Phys. Chem. Ref. Data* **16**, 471 (1987).
- <sup>43</sup>M. W. Chase, Jr., C. A. Davies, J. R. Downey, Jr., D. J. Frurip, R. A. McDonald, and A. N. Syverud, *JANAF Thermochemical Tables*, 3rd ed. J. Phys. Chem. Ref. Data **14**, Suppl. 1 (1985).
- <sup>44</sup>F. R. Cruickshank and S. W. Benson, *J. Phys. Chem.* **73**, 733 (1969).
- <sup>45</sup>M. E. Jacox, *Chem. Phys.* **59**, 213 (1981).
- <sup>46</sup>J. C. Traeger and R. G. Mc Loughlin, *J. Am. Chem. Soc.* **103**, 3647 (1981).
- <sup>47</sup>J. B. Pedley, R. D. Naylor, and S. P. Kirby, *Thermochemical Data of Organic Compounds*, 2nd ed. (Chapman and Hall, New York, 1986).
- <sup>48</sup>B. Ruscic and J. Berkowitz, *Prepr. Pap.-Am. Chem. Soc., Div. Fuel Chem.* **36**, 1571 (1991).
- <sup>49</sup>*TRC Thermodynamic Tables Nonhydrocarbons* (Texas A and M University System, 1986).
- <sup>50</sup>M. S. Gordon and D. G. Truhlar, *J. Am. Chem. Soc.* **108**, 5412 (1968).
- <sup>51</sup>E. Feenberg, *Ann. Phys. (N.Y.)* **3**, 292 (1958); S. Wilson, *Int. J. Quantum Chem.* **18**, 905 (1980).
- <sup>52</sup>W. B. DeMore, S. P. Sander, D. M. Golden, R. F. Hampson, M. J. Kurylo, C. J. Howard, A. R. Ravishankara, C. E. Kolb, and M. J. Molina, Evaluation No. 12, JPL Publication 97-4, NASA and JPL, January 15, 1997.
- <sup>53</sup>M. Sana, G. Leroy, D. Peeters, and E. Younang, *J. Mol. Struct. (Theochem)* **151**, 325 (1987).
- <sup>54</sup>M. Sana, G. Leroy, D. Peeters, and C. Wilante, *J. Mol. Struct. (Theochem)* **164**, 249 (1988).
- <sup>55</sup>T. Shimanouchi, *Tables of Molecular Vibrational Frequencies* (National Bureau of Standards, Washington, DC, 1972).
- <sup>56</sup>L. H. Jones and R. S. McDowell, *J. Mol. Spectrosc.* **3**, 632 (1959).
- <sup>57</sup>M. E. Jacox, *J. Phys. Chem. Ref. Data* **13**, 945 (1984).
- <sup>58</sup>C. W. Bauschlicher and H. Partridge, *Chem. Phys. Lett.* **215**, 451 (1993).
- <sup>59</sup>D. D. Wagman, W. H. Evans, V. B. Parker, S. H. Schumm, I. Halow, S. M. Bailey, K. L. Churney, and R. L. Nuttall, *J. Phys. Chem. Ref. Data* **11**, Suppl. 1 (1982).
- <sup>60</sup>O. Dobis and S. W. Benson, *Int. J. Chem. Kinet.* **19**, 691 (1987).
- <sup>61</sup>L. A. Curtiss, P. C. Redfern, K. Raghavachari, V. Rassolov, and J. A. Pople, *J. Chem. Phys.* **110**, 4703 (1999).
- <sup>62</sup>L. A. Curtiss, K. Raghavachari, P. C. Redfern, and J. A. Pople, *J. Chem. Phys.* **106**, 1063 (1997); see also L. A. Curtiss, L. D. Kock, and J. A. Pople, *ibid.* **95**, 4040 (1991).
- <sup>63</sup>A. G. Baboul, L. A. Curtiss, P. C. Redfern, and K. Raghavachari, *J. Chem. Phys.* **110**, 7650 (1999).
- <sup>64</sup>A. V. Marenich and J. E. Boggs, *J. Chem. Phys.* **119**, 10105 (2003).
- <sup>65</sup>B. J. Smith and L. Radom, *J. Am. Chem. Soc.* **115**, 4885 (1993).
- <sup>66</sup>M. L. Ma, B. J. Smith, J. A. Pople, and L. Radom, *J. Am. Chem. Soc.* **113**, 7903 (1991).
- <sup>67</sup>W. Tao, R. B. Klemm, F. L. Nesbitt, and L. J. Stief, *J. Phys. Chem.* **96**, 104 (1992).
- <sup>68</sup>W. Tsang, *Int. J. Chem. Kinet.* **8**, 173 (1976).
- <sup>69</sup>P. J. Bruna and F. Grein, *J. Phys. Chem. A* **102**, 3141 (1998).
- <sup>70</sup>M. E. Jacox, *Vibrational and Electronic Energy Levels of Polyatomic Transient Molecules*, *J. Phys. Chem. Ref. Data Monogr.* 3 (1994).
- <sup>71</sup>M. E. Jacox, *J. Phys. Chem. Ref. Data* **32**, 1 (2003).
- <sup>72</sup>B. J. McBride, M. Zehe, and S. Gordon, *NASA Lewis/Glenn Thermodynamic Database*, in conjunction with the on-line interactive program *Properties From Coefficients* (NASA Lewis Research Center, Cleveland, OH, 2002) (see also <http://cea.grc.nasa.gov/index.html>)

7.2.2. CH<sub>3</sub>CO Radical

## 7.2.2. Acetyl radical

3170-69-2

CH <sub>3</sub> CO( <sup>2</sup> A')	C <sub>s</sub> (σ <sub>ext</sub> = 1)
Δ <sub>f</sub> H°(298.15 K) = -10.3 ± 1.8 kJ mol <sup>-1</sup>	Δ <sub>f</sub> H°(0 K) = -3.6 ± 1.8 kJ mol <sup>-1</sup>
C <sub>p</sub> °(298.15 K) = 50.785 J K <sup>-1</sup> mol <sup>-1</sup>	H°(298.15 K) - H°(0 K) = 12.385 kJ mol <sup>-1</sup>
S°(298.15 K) = 267.448 J K <sup>-1</sup> mol <sup>-1</sup>	p° = 100 000 Pa (1 bar)

## Literature Data for the Enthalpy of Formation at 298.15 K

Δ <sub>f</sub> H°/kJ mol <sup>-1</sup>	Authors and Reference	Method <sup>a</sup>	Comments
<b>Measurements</b>			
-11.2 <sup>b</sup> ± 5 <sup>c</sup>	Watkins and Word (1974) <sup>1</sup>	KE	(1a)
-18.8 ± 9.8 <sup>c</sup>	Holmes and Lossing (1984) <sup>2</sup>	EIMS-PIC	(1b)
-13.8 ± 6.0	Tsang (1984) <sup>3</sup>	KE	(1c)
-22.6 ± 14.3 <sup>c</sup>	Nimlos <i>et al.</i> (1989) <sup>4</sup>	PES-NIC	(1d)
-10.0 ± 1.2	Niiranen <i>et al.</i> (1992) <sup>5</sup>	KE	(1e)
-6 ± 15	Mousavipour and Pacey (1996) <sup>6</sup>	PY	(1f)
<b>Computations</b>			
-17.8 ± 8.4	Francisco and Abersold (1991) <sup>7</sup>	PMP4SDTQ	(1g)
-9.2 ± 2.9	Bauschlicher (1994) <sup>8</sup>	RCCSD(T)	(1h)
-7.5 ± 4.4 <sup>c</sup>	Zachariah <i>et al.</i> (1996) <sup>9</sup>	BAC-MP4	(1i)
-10.5 ± 13 <sup>c</sup>	Curtiss <i>et al.</i> (1998) <sup>10</sup>	CBS-Q	(1j)
-10.5 ± 7.9 <sup>c</sup>	Curtiss <i>et al.</i> (1998) <sup>11</sup>	G3	(1k)
-10.3 <sup>b</sup> ± 5 <sup>c</sup>	Viskolcz and Bérces (2000) <sup>12</sup>	G2(MP2,SVP)	(1l)
-13.0 ± 3.1 <sup>c</sup>	Parthiban and Martin (2001) <sup>13</sup>	W1	(1m)
-11.6 ± 7.8 <sup>c</sup>	Janoschek and Rossi (2002) <sup>14</sup>	G3MP2B3	(1n)
<b>Reviews and Evaluations</b>			
-18.8	NBS (1982) <sup>15</sup>	TT-U	(1o)
-24.3 ± 1.7	McMillen and Golden (1982) <sup>16</sup>	CDE	(1p)
-10.0 ± 1.3	Berkowitz <i>et al.</i> (1994) <sup>17</sup>	CDE	(1q)
-12 ± 3	Tsang (1996) <sup>18</sup>	CDE	(1r)
-11.1 ± 1.8	Traeger and Kompe (1996) <sup>19</sup>	CDE	(1s)
-12.0 ± 3.0	NIST CCCBDB (1999) <sup>20</sup>	TT-A	(1t)
-10.0 ± 1.2	Atkinson <i>et al.</i> (2000) <sup>21</sup>	TT-A	(1u)
-10.0 ± 1.2	Kerr and Stocker (2000) <sup>22</sup>	TT-A	(1v)
-10.0	Burcat (2001) <sup>23</sup>	TT-A	(1w)
-10.0 ± 1.2	Sander <i>et al.</i> (2003) <sup>24</sup>	TT-A	(1x)
-12.0 ± 3.0	NIST WebBook (2003) <sup>25</sup>	TT-A	(1y)

<sup>a</sup>EIMS-PIC: positive ion cycle based on combining electron impact mass-spectrometric measurements of appearance energy ( $E_{ap}$ ) from a stable molecule with ionization energy ( $E_i$ ) of the radical; PES-NIC: negative ion cycle based on combining the electron affinity of a radical with the gas-phase acidity of hydrogenated parent molecule; KE: kinetic equilibrium study; PY: flow pyrolysis study; CDE: critical data evaluation; TT-U: unannotated tabulation of thermodynamic data; TT-A: annotated tabulation of thermodynamic data.

<sup>b</sup>The quoted value was either not given explicitly by the author(s) or it was recalculated using auxiliary thermochemical values that differ from those used by the original authors; see individual comments for additional details.

<sup>c</sup>The uncertainty was either not given explicitly by the original author(s) or it has been modified; see individual comments for further explanations.

## Comments on the Enthalpies of Formation

(1a) Reaction CH<sub>3</sub> + CO → CH<sub>3</sub>CO studied in the forward and reverse direction by photolyzing azomethane with 350–380 nm light from a medium-pressure mercury-arc in the presence of carbon monoxide and analyzing the products by gas-liquid chromatography. From measurements of the acetyl radical yield at 700–2100 Torr and 260–413 K, ex-

trapolation to infinite pressure yielded the rate coefficients for methyl addition to CO and acetyl radical decomposition of  $k_f = 1.59 \times 10^{11} \exp(-25 \text{ kJ mol}^{-1}/RT) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  and  $k_r = 3.18 \times 10^{13} \exp(-72 \text{ kJ mol}^{-1}/RT) \text{ s}^{-1}$ , respectively.

From the measured activation energies,  $E_{a,f} - E_{a,r} = -47 \text{ kJ mol}^{-1}$  ( $\Delta_f H^\circ_{298} = -49 \text{ kJ mol}^{-1}$ ) is obtained. Using this reaction enthalpy and enthalpies of formation for the

remaining species, the second-law value of  $\Delta_f H^\circ_{298}(\text{CH}_3\text{CO}) = -17 \pm 3 \text{ kJ mol}^{-1}$  was estimated. However, a recalculation using the preferred value from the current compilation,  $\Delta_f H^\circ_{298}(\text{CH}_3) = 146.7 \pm 0.3 \text{ kJ mol}^{-1}$  in conjunction with the standard value<sup>26</sup>  $\Delta_f H^\circ_{298}(\text{CO}) = -110.53 \pm 0.17 \text{ kJ mol}^{-1}$ , results in  $\Delta_f H^\circ_{298}(\text{CH}_3\text{CO}) = -12.8 \pm 3 \text{ kJ mol}^{-1}$ .

From the experimental rate coefficient expressions, the room temperature equilibrium constant of  $K(298.15 \text{ K}) = 8.67 \times 10^5 \text{ cm}^3 \text{ mol}^{-1}$  is obtained. This value, together with the presently adopted values  $S^\circ_{298}(\text{CH}_3\text{CO}) = 267.448 \text{ J K}^{-1} \text{ mol}^{-1}$ ,  $S^\circ_{298}(\text{CH}_3) = 194.008 \text{ J K}^{-1} \text{ mol}^{-1}$ , and  $\Delta_f H^\circ_{298}(\text{CH}_3) = 146.7 \pm 0.3 \text{ kJ mol}^{-1}$ , in conjunction with the CODATA recommended<sup>26</sup> values  $S^\circ_{298}(\text{CO}) = 197.660 \text{ J mol}^{-1} \text{ K}^{-1}$  and  $\Delta_f H^\circ_{298}(\text{CO}) = -110.53 \pm 0.17 \text{ kJ mol}^{-1}$ , leads to the third-law value of  $\Delta_f H^\circ_{298}(\text{CH}_3\text{CO}) = -9.6 \pm 3 \text{ kJ mol}^{-1}$ . The value given in the table is an average of the second-law and third-law values.

(1b) Electron impact mass-spectrometric measurements of appearance energies of various fragments from five precursors. These were combined with the literature electron-impact values<sup>27–31</sup> for ions or neutral fragments, together with enthalpies of formation for the parent compounds that are either tabulated<sup>32</sup> or estimated from group-additivity, to give the reported enthalpy of formation,  $\Delta_f H^\circ_{298}(\text{CH}_3\text{CO}) = -18.8 \text{ kJ mol}^{-1}$  ( $-4.5 \text{ kcal mol}^{-1}$ ). This value is the average of the derived values of  $-5.2$ ,  $-4.8$ ,  $-4.5$ ,  $-4.2$ , and  $-3.9 \text{ kcal mol}^{-1}$ . The authors do not give an explicit uncertainty estimate. The uncertainty initially assigned to this measurement ( $\pm 6 \text{ kJ mol}^{-1}$ ) attempted to reflect the general disparity between various measurements of the same species obtained by this method. However, as a consequence of the linear analysis discussed in conjunction with the selection of the preferred value, the final uncertainty assigned to this measurement is  $\pm 9.8 \text{ kJ mol}^{-1}$ .

(1c) Aliphatic ketones decomposed to acetyl radicals in comparative rate single pulse shock tube experiments. Reaction  $\text{C}_6\text{H}_{10} \rightarrow 1,3\text{-C}_4\text{H}_6 + \text{C}_2\text{H}_4$  was used as internal standard for which the rate expression is well established:<sup>33</sup>  $k = 10^{15.15} \exp(-33.500/T) \text{ s}^{-1}$ . Gas chromatography with flame ionization detection was used for product analysis, with toluene used to scavenge reactive radicals. Investigation of the reaction  $3\text{-methyl-pentanone-2} \rightarrow \text{CH}_3\text{CO} + s\text{-C}_4\text{H}_9$  at  $960\text{--}1170 \text{ K}$  temperatures and  $1.5\text{--}6.0 \text{ atm}$  pressures resulted in the rate expression  $k = 10^{16.4} \exp(-38.300/T) \text{ s}^{-1}$ . Study of the decomposition reaction  $5\text{-methyl-hexanone-2} \rightarrow \text{CH}_3\text{CO} + i\text{-C}_4\text{H}_9$  gave  $k = 10^{16.6} \exp(-40.600/T) \text{ s}^{-1}$ . Assuming that the reverse combination processes have zero activation energies in concentration units, the enthalpy of formation for  $\text{CH}_3\text{CO}$  at  $1100 \text{ K}$  was derived using the relation  $\Delta_f H^\circ(\text{CH}_3\text{CO}) + \Delta_f H^\circ(\text{alkyl radical}) - \Delta_f H^\circ(\text{ketone}) = E_a - RT$ , where  $E_a$  is the activation energy of decomposition and  $\Delta_f H^\circ(\text{ketone})$  is estimated<sup>34</sup> from  $\Delta_f H^\circ(\text{ketone}) - \Delta_f H^\circ(\text{alkane}) = -106.7 \pm 2 \text{ kJ}$ . Then, upon substitution and correction to  $298.15 \text{ K}$ ,  $\Delta_f H^\circ_{298}(\text{CH}_3\text{CO}) = -13.8 \text{ kJ mol}^{-1}$  was obtained.

(1d) An electron affinity of  $E_{\text{ea}}(\text{CH}_3\text{CO}) = 0.423 \pm 0.037 \text{ eV}$

for the acetyl radical extracted from the photoelectron spectrum of the  $\text{CH}_3\text{CO}^-$  anion combined with the gas phase acidity of DePuy *et al.*<sup>35</sup> of  $\Delta H_{\text{acid}}(\text{CH}_3\text{CO}-\text{H}) = 1631.8 \pm 8.4 \text{ kJ mol}^{-1}$  and an enthalpy of formation for  $\text{CH}_3\text{CHO}$  of  $-165.8 \pm 0.4 \text{ kJ mol}^{-1}$  from Pedley and Rylance<sup>32</sup> gave  $\Delta_f H^\circ_{298}(\text{CH}_3\text{CO}) = -22.6 \pm 8.8 \text{ kJ mol}^{-1}$ . However, as a consequence of the linear analysis discussed in conjunction with the selection of the preferred value, the final uncertainty assigned to this measurement is  $\pm 14.3 \text{ kJ mol}^{-1}$ . These authors also provide a structure and vibrational frequencies as obtained from HF/6-311++G\*\* *ab initio* calculations. These were subsequently used by Niiranen *et al.*<sup>5</sup> [see (1e) below] to calculate the partition function for acetyl radical. (1e) The kinetics of the reaction  $\text{CH}_3\text{CO} + \text{HBr} \rightarrow \text{CH}_3\text{CHO} + \text{Br}$  studied using a tubular reactor coupled to a photoionization mass spectrometer.  $\text{CH}_3\text{CO}$  was produced by laser photolysis and radical decays were monitored in time-resolved experiments. Experiments over the temperature range of  $300\text{--}400 \text{ K}$  gave the Arrhenius expression  $k_f = (6.4 \pm 3.6) \times 10^{-13} \exp[(4.45 \pm 1.50) \text{ kJ mol}^{-1}/RT] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . This result, combined with the rate coefficient expression for the reverse reaction of  $k_r = (1.51 \pm 0.20) \times 10^{-11} \exp(-364 \pm 41)/T \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  derived by Nicovich *et al.*<sup>36</sup> in the temperature range of  $255\text{--}400 \text{ K}$ , was used to obtain the second-law and third-law enthalpy of formation of  $\text{CH}_3\text{CO}$ . These authors also calculated the thermochemical functions of  $\text{CH}_3\text{CO}$  based on bond angles and vibrational frequencies of  $\text{CH}_3\text{CO}$  that were given by Nimlos *et al.*<sup>4</sup> [see (1d) above]. The torsion motion was treated as a hindered rotor with a three-cycle sinusoidal internal rotational barrier ( $92.0 \text{ cm}^{-1}$ , calculated from the torsional frequency  $94 \text{ cm}^{-1}$  of Nimlos *et al.*) and its contribution was estimated using the tables of Pitzer and Gwinn.<sup>37</sup>

In the second-law calculation, the enthalpy change in the reaction at  $343 \text{ K}$  is obtained directly from the difference of the Arrhenius activation energies between the forward and reverse reactions,  $\Delta_r H^\circ(343 \text{ K}) = E_{\text{a,f}} - E_{\text{a,r}} = -7.5 \pm 1.6 \text{ kJ mol}^{-1}$ . By using existing heat capacities<sup>38</sup> for  $\text{CH}_3\text{CHO}$ ,  $\text{HBr}$ , and  $\text{Br}$ , and their own calculated heat capacities for  $\text{CH}_3\text{CO}$ , corrections to  $\Delta_r H^\circ(343 \text{ K})$  were made to obtain  $\Delta_r H^\circ(298.15 \text{ K}) = -7.3 \pm 1.6 \text{ kJ mol}^{-1}$ . This, together with the enthalpies of formation of the remaining species involved,<sup>39</sup> gave  $\Delta_f H^\circ_{298}(\text{CH}_3\text{CO}) = -10.3 \pm 1.6 \text{ kJ mol}^{-1}$ .

In the third-law calculation, the free energy change in the reaction at  $298.15 \text{ K}$  was obtained from the equilibrium constant  $K = k_f/k_r$  (which was calculated using the Arrhenius expressions given above):  $\Delta_r G^\circ(298.15 \text{ K}) = -RT \ln(k_f/k_r) = (0.35 \pm 0.70) \text{ kJ mol}^{-1}$ . The entropy change of the reaction was obtained from their own separately calculated entropy for  $\text{CH}_3\text{CO}$  and calculated molar entropies<sup>40,41</sup> of the remaining species:  $\Delta_r S^\circ(298.15 \text{ K}) = -27.0 \pm 3.0 \text{ J mol}^{-1} \text{ K}^{-1}$ . Thus, the enthalpy change of  $\Delta_r H^\circ(298.15 \text{ K}) = \Delta_r G^\circ(298.15 \text{ K}) + T\Delta_r S^\circ(298.15 \text{ K}) = -7.7 \pm 1.1 \text{ kJ mol}^{-1}$  was obtained. Finally, this together with the enthalpies of formation of  $\text{CH}_3\text{CHO}$ ,  $\text{HBr}$ , and  $\text{Br}$  from Atkinson *et al.*<sup>39</sup> gave  $\Delta_f H^\circ_{298}(\text{CH}_3\text{CO}) = -9.9 \pm 1.1 \text{ kJ mol}^{-1}$ . The authors note the closeness of the results obtained by second and

third-law treatment and recommend the enthalpy of formation  $\Delta_f H^\circ_{298}(\text{CH}_3\text{CO}) = -10.0 \pm 1.2 \text{ kJ mol}^{-1}$  as the weighted average of the second-law and third-law determination.

(lf) The rate of decomposition  $(\text{CH}_3)_2\text{CO} \rightarrow \text{CH}_3 + \text{CH}_3\text{CO}$  studied in the flow pyrolysis of acetone at 825–940 K and 10–180 Torr using gas chromatography to measure product yields. The rate coefficient for the decomposition reaction was determined from the sum of the yields of the termination products (ethane, butanone, and 2,5-hexanedione). The high-pressure limiting rate coefficient expression (obtained from a nonlinear least-squares fit to the experimental data using the Troe factorization procedure<sup>42</sup>) was found to be  $k_f = 10^{17.9 \pm 0.8} \exp[-(353 \pm 14) \text{ kJ mol}^{-1}/RT] \text{ s}^{-1}$ . Assuming that the reverse combination reaction has zero activation energy, the internal energy change and enthalpy change for the decomposition reaction at the middle of the temperature range are  $\Delta_r E(882 \text{ K}) = 353 \pm 15 \text{ kJ}$  and  $\Delta_r H^\circ(882 \text{ K}) = 360 \pm 15 \text{ kJ mol}^{-1}$ , respectively. With (unspecified) literature values of heat capacities,  $\Delta_r H^\circ(298.15 \text{ K}) = 358 \pm 15 \text{ kJ mol}^{-1}$  is obtained which combined with enthalpies of formation for acetone<sup>43</sup> and methyl<sup>41</sup> yields  $\Delta_f H^\circ_{298}(\text{CH}_3\text{CO}) = -6 \pm 15 \text{ kJ mol}^{-1}$ . It is to be noted, however, that a lower activation energy of  $E_{\text{act}} = 342 \pm 12 \text{ kJ mol}^{-1}$  has been obtained for the acetone decomposition reaction in shock tube experiments,<sup>44</sup> which corresponds to an acetyl radical enthalpy of formation lower by about  $11 \text{ kJ mol}^{-1}$ . Therefore, the flow pyrolysis result is probably an upper limit.

(lg) *Ab initio* molecular orbital calculations at various levels of theory. Isodesmic reactions  $\text{CH}_3\text{CO} + \text{CH}_4 \rightarrow \text{HCO} + \text{CH}_3\text{CH}_3$  (1) and  $\text{CH}_3\text{CO} + \text{CH}_3\text{Cl} \rightarrow \text{ClCO} + \text{CH}_3\text{CH}_3$  (2) were studied. The computed enthalpy change at the PMP4SDTQ/6-311++G(d,p) level of theory for reactions (1) and (2), with geometries optimized at the MP2/6-311G(d,p) level, were  $13.0$  and  $-2.2 \text{ kJ mol}^{-1}$ , respectively. Using experimental enthalpies of formation for the rest of species involved,<sup>15,41,45–48</sup> the values of  $\Delta_f H^\circ_{298}(\text{CH}_3\text{CO}) = -20.5 \text{ kJ mol}^{-1}$  and  $\Delta_f H^\circ_{298}(\text{CH}_3\text{CO}) = -15.1 \text{ kJ mol}^{-1}$  were derived from the two computed reaction enthalpies, respectively. The average of  $\Delta_f H^\circ_{298}(\text{CH}_3\text{CO}) = -17.8 \text{ kJ mol}^{-1}$  is obtained from the two determinations.

(lh) *Ab initio* molecular orbital calculations at the CCSD(T)/cc-pVTZ level using MP2/6-311++G(3df,2p) geometries. The isodesmic reaction  $\text{CH}_3 + \text{CH}_3\text{CHO} \rightarrow \text{CH}_4 + \text{CH}_3\text{CO}$  was studied and  $-70.29 \text{ kJ mol}^{-1}$  was obtained for the reaction enthalpy without zero-point energy. By correcting this result for the  $0.50 \text{ kJ mol}^{-1}$  change between the cc-pVTZ and the cc-pVQZ basis set,  $-70.79 \text{ kJ mol}^{-1}$  was obtained for the reaction enthalpy. The zero-point energy contribution to the reaction was computed to be  $7.49 \text{ kJ mol}^{-1}$  using scaled MP2 frequencies. Combining the resulting estimate for the reaction enthalpy and the adopted C–H bond dissociation energy in  $\text{CH}_4$  of  $432.4 \pm 0.8 \text{ kJ mol}^{-1}$ , which was based on experimental determinations by Chupka<sup>49</sup> and by Dobis and Benson,<sup>50</sup> yielded an aldehyde C–H bond dissociation energy of  $D_0(\text{CH}_3\text{C}(\text{O})\text{--H}) = 369.1 \pm 2.4 \text{ kJ mol}^{-1}$ .

The indicated uncertainty reflects the estimates for the uncertainty in the calculated reaction enthalpy ( $0.8 \text{ kJ mol}^{-1}$ ), the uncertainty in the zero-point correction ( $0.7 \text{ kJ mol}^{-1}$ ) and the uncertainty in the  $\text{CH}_4$  bond dissociation energy ( $0.8 \text{ kJ mol}^{-1}$ ).

When the correction to 298.15 K was computed, the  $\text{CH}_3$  motion was treated as a hindered rotation. The best estimate for the barrier to  $\text{CH}_3$  rotation was  $4.44$  and  $2.01 \text{ kJ mol}^{-1}$  in  $\text{CH}_3\text{CHO}$  and  $\text{CH}_3\text{CO}$ , respectively. Thus,  $1.71$  and  $1.43 \text{ kJ mol}^{-1}$  was obtained for the contribution of this rotation to  $H^\circ(298.15 \text{ K}) - H^\circ(0 \text{ K})$  for  $\text{CH}_3\text{CHO}$  and  $\text{CH}_3\text{CO}$ , respectively. The remaining modes were treated as harmonic oscillators, leading to the total corrections of  $[H^\circ(298.15 \text{ K}) - H^\circ(0 \text{ K})](\text{CH}_3\text{CHO}) = 12.732 \text{ kJ mol}^{-1}$  and  $[H^\circ(298.15 \text{ K}) - H^\circ(0 \text{ K})](\text{CH}_3\text{CO}) = 12.372 \text{ kJ mol}^{-1}$ . Using known enthalpies of formation<sup>15</sup> and enthalpy increments for the other species involved, the computed RCCSD(T) reaction enthalpy leads to  $\Delta_f H^\circ_0(\text{CH}_3\text{CO}) = -2.3 \pm 2.5 \text{ kJ mol}^{-1}$  and  $\Delta_f H^\circ_{298}(\text{CH}_3\text{CO}) = -9.2 \pm 2.9 \text{ kJ mol}^{-1}$ . On the basis of careful estimation of the errors in the computed results, it was concluded that all reported enthalpies of formation below  $-3.0 \text{ kcal mol}^{-1} = -12.6 \text{ kJ mol}^{-1}$  can be ruled out.

(li) BAC-MP4 *ab initio* calculations. The originally quoted uncertainty of  $\pm 4.4 \text{ kJ mol}^{-1}$  was multiplied by a factor of 2 to bring it closer to the desired 95% confidence limit.

(lj) CBS-Q calculation. The value listed in the table is converted from  $-2.5 \text{ kcal mol}^{-1}$ . The reported average absolute deviation of  $1.57 \text{ kcal mol}^{-1}$  was multiplied by 2 to bring it closer to the desired 95% confidence limit. The equivalent CBS-q and CBS-4 enthalpies of formation are  $-5.9 \pm 18 \text{ kJ mol}^{-1}$  ( $-1.4 \text{ kcal mol}^{-1}$ ) and  $-15.5 \pm 26 \text{ kJ mol}^{-1}$  ( $-3.7 \text{ kcal mol}^{-1}$ ), where the uncertainties have been obtained in an analogous way.

(lk) G3 *ab initio* calculation. The value listed in the table is converted from  $-2.5 \text{ kcal mol}^{-1}$ . The uncertainty quoted in the table corresponds approximately to 95% confidence limits, based on twice the average absolute deviation of  $0.94 \text{ kcal mol}^{-1}$  for the enthalpies in the G2/97 test set, which roughly corresponds to 1 s.d. At the G3(MP2) level of theory<sup>51</sup>  $\Delta_f H^\circ_{298}(\text{CH}_3\text{CO}) = -10.0 \pm 9.9 \text{ kJ mol}^{-1}$  ( $-2.4 \text{ kcal mol}^{-1}$ ), where the quoted uncertainty has been derived in a similar fashion as for the G3 value. At the G2 level of theory<sup>52</sup>  $\Delta_f H^\circ_{298}(\text{CH}_3\text{CO}) = -11.7 \pm 13.1 \text{ kJ mol}^{-1}$  ( $-2.8 \text{ kcal mol}^{-1}$ ). Note that the independent G2 value of Zhao *et al.*<sup>53</sup> ( $-12.2 \text{ kJ mol}^{-1}$ ,  $-2.9 \text{ kcal mol}^{-1}$ ) differs only by a round-off of  $0.1 \text{ kcal mol}^{-1}$ .

(ll) G2(MP2,SVP)/MP2(full)/6-31G(d) method. The atomization energy for  $\text{CH}_3\text{CO}$  was obtained, and combined with the experimental atomic enthalpies of formation<sup>41</sup> resulted in  $\Delta_f H^\circ_{298}(\text{CH}_3\text{CO}) = -12.6 \text{ kJ mol}^{-1}$ . In addition, the reaction enthalpy at 298.15 K of the isodesmic reaction  $\text{CH}_3 + \text{CH}_3\text{CHO} \rightarrow \text{CH}_4 + \text{CH}_3\text{CO}$  was studied at the CBS-4//HF/3-21G\* level of theory. From the computed  $\Delta_r H^\circ(298.15 \text{ K}) = -63.5 \text{ kJ mol}^{-1}$  and the enthalpies of formation for the rest of participating species,<sup>54,18</sup>  $\Delta_f H^\circ_{298}(\text{CH}_3\text{CO}) = -7.9 \text{ kJ mol}^{-1}$  was obtained. The



enthalpy of formation listed in the table is an average of the two values.

(1m) W1 *ab initio* computation. The uncertainty quoted in the table corresponds approximately to 95% confidence limits based on twice the average absolute deviation of 0.37 kcal mol<sup>-1</sup> for the W1 test set, which corresponds roughly to 1 s.d.

(1n) G3(MP2)//B3LYP *ab initio* calculations for 32 selected free radicals. The uncertainty given in the table corresponds approximately to 95% confidence limits based on twice the quoted average absolute deviation of 3.9 kJ mol<sup>-1</sup> for the calculated set of radicals, which corresponds roughly to 1 s.d. Note that the average absolute deviation for all enthalpies in the G2/97 test set using the same method is very slightly larger:<sup>55</sup> 4.7 kJ mol<sup>-1</sup> [see also (1k) above].

(1o) Critical data evaluation, but does not provide a pedigree of the selected value nor does it quote uncertainties.

(1p) Recommended value from extensive evaluation of data (mainly kinetic determinations) published till 1981. The recommended value is based on two previous reviews.

(1q) Critical data evaluation of R–H bond dissociation energies based on three methods: kinetic determinations, positive ion cycle determinations from photoelectron/photoionization measurements and negative ion cycle determinations from photoelectron measurements of negative ions combined with gas phase acidities. The recommended value is based on the kinetic determination of Niiranen *et al.*<sup>5</sup> [see (1e) above].

(1r) Critical data evaluation for selected free radicals based on kinetic measurements. The recommended value is an average of the enthalpies of formation reported by Watkins and Word,<sup>1</sup> Tsang,<sup>3</sup> and Niiranen *et al.*<sup>5</sup> [see (1a), (1c), and (1e) above].

(1s) Appearance energy measurements<sup>56</sup>  $E_{\text{ap}}(\text{CH}_3\text{CO}^+/\text{(CH}_3)_2\text{CO}) = 1001.4 \pm 1.0 \text{ kJ mol}^{-1}$ ,  $E_{\text{ap}}(\text{CH}_3\text{CO}^+/\text{(CH}_3(\text{CO})\text{C}_2\text{H}_5)) = 995.7 \pm 1.0 \text{ kJ mol}^{-1}$ , and  $E_{\text{ap}}(\text{CH}_3\text{CO}^+/\text{(CH}_3(\text{CO})\text{OH})) = 1113.4 \pm 1.0 \text{ kJ mol}^{-1}$ . With these results an average enthalpy of formation of  $\Delta_f H^\circ_{298}(\text{CH}_3\text{CO}^+) = 655.5 \pm 0.8 \text{ kJ mol}^{-1}$  for the acetyl cation was obtained. The authors unfortunately had no reliable experimental value available for the adiabatic ionization energy of the acetyl radical, however, the appearance energy for the formation of  $\text{CH}_3\text{CO}^+ + \text{CH}_3\text{CO}$  from biacetyl<sup>56</sup> (953.3 kJ mol<sup>-1</sup>) provided a good estimate as this process is free from any competitive shift. From this and the enthalpy of formation of the  $\text{CH}_3\text{CO}^+$  cation, the value of  $\Delta_f H^\circ_{298}(\text{CH}_3\text{CO}) = -11.1 \pm 1.8 \text{ kJ mol}^{-1}$  was derived. Since the reverse process of biacetyl fragmentation may have an activation energy above zero, this determination of  $\Delta_f H^\circ_{298}(\text{CH}_3\text{CO})$  can only be regarded as an upper limit.

(1t) The compilation lists theoretical results at various levels of theory, but also makes a reference to one experimental benchmark. The quoted experimental benchmark value is from Tsang<sup>18</sup> [see (1r) above].

(1u) Critical evaluation of atmospherically relevant kinetic rates. Their table of enthalpy data lists the value reported by Kerr and Stocker,<sup>22</sup> who in turn recommend the value of Niiranen *et al.*<sup>5</sup> [see (1e) above].

(1v) Thermodynamic data compilation. The preferred value is that reported by Niiranen *et al.*<sup>5</sup> [see (1e) above].

(1w) Thermodynamic database for combustion. The preferred value is that reported by Niiranen *et al.*<sup>5</sup> [see (1e) above].

(1x) Critical evaluation of atmospherically relevant kinetic data. The quoted value is from Berkowitz *et al.*<sup>17</sup> [see (1q) above], who in turn base their value on Niiranen *et al.*<sup>5</sup> [see (1e) above].

(1y) An unevaluated tabulation of available values from other sources. The source for the listed value is quoted as Tsang<sup>18</sup> [see (1r) above].

### Preferred Value of the Enthalpy of Formation

$$\Delta_f H^\circ(298.15 \text{ K}) = -10.3 \pm 1.8 \text{ kJ mol}^{-1}$$

$$\Delta_f H^\circ(0 \text{ K}) = -3.6 \pm 1.8 \text{ kJ mol}^{-1}$$

The reported experimental enthalpies of formation show significant scatter. The three results of kinetic equilibrium studies are in reasonably good agreement with each other and produce a weighted average of  $\Delta_f H^\circ_{298}(\text{CH}_3\text{CO}) = -10.2 \pm 2.3 \text{ kJ mol}^{-1}$ . The weighted average of all calculations produces  $-10.7 \pm 2.1 \text{ kJ mol}^{-1}$ . The weighted average of all six listed experimental values is similar, albeit it has a somewhat larger uncertainty:  $-10.7 \pm 2.7 \text{ kJ mol}^{-1}$ . However, a linear analysis indicates that the two most negative values ( $-18.8 \pm 6$  by Holmes and Lossing<sup>2</sup> and  $-22.6 \pm 8.8$  by Nimlos *et al.*<sup>4</sup>) deviate consistently from the weighted averages significantly more than their originally assigned uncertainties would suggest, and that reconciliation with the other data can be achieved if amplified uncertainties of  $\pm 9.8$  and  $\pm 14.3 \text{ kJ mol}^{-1}$ , respectively, are assumed.

The preferred value is the weighted average of all listed experimental measurements, taking into account the noted amplified uncertainties for the two most negative values.

The preferred value corresponds to the C–H bond dissociation energy in acetaldehyde  $D_{298}(\text{CH}_3\text{C}(\text{O})-\text{H}) = 373.5 \pm 1.8 \text{ kJ mol}^{-1}$  ( $367.6 \pm 1.8 \text{ kJ mol}^{-1}$  at 0 K) as well as the C–C bond dissociation energy in acetyl  $D_{298}(\text{CH}_3-\text{CO}) = 46.5 \pm 1.8 \text{ kJ mol}^{-1}$  ( $39.8 \pm 1.8 \text{ kJ mol}^{-1}$  at 0 K). These produce the listed enthalpy when used together with auxiliary thermochemical values as follows:  $\Delta_f H^\circ_{298}(\text{CH}_3\text{C}(\text{O})\text{H}) = -165.8 \pm 0.4 \text{ kJ mol}^{-1}$  is adopted from Pedley and Rylance<sup>32</sup> (note that, without giving an uncertainty, the NBS Tables<sup>15</sup> list a very similar value of  $-166.19 \text{ kJ mol}^{-1}$ , Cox and Pilcher<sup>54</sup> quote  $-166.23 \pm 0.50 \text{ kJ mol}^{-1}$  based on Dolliver *et al.*,<sup>57</sup> while Atkinson *et al.*<sup>21</sup> give the value by Pedley and Rylance<sup>32</sup> of  $-165.8 \pm 0.4 \text{ kJ mol}^{-1}$  but quote also Cox and Pilcher<sup>54</sup> as the source),  $[H^\circ(298.15 \text{ K}) - H^\circ(0 \text{ K})](\text{CH}_3\text{CHO}) = 12.732 \text{ kJ mol}^{-1}$  as obtained by Bauschlicher,<sup>8</sup>  $\Delta_f H^\circ_{298}(\text{CH}_3) = 146.7 \pm 0.3 \text{ kJ mol}^{-1}$  and  $[H^\circ(298.15 \text{ K}) - H^\circ(0 \text{ K})](\text{CH}_3) = 10.366 \text{ kJ mol}^{-1}$  as determined in the

present compilation,  $[H^\circ(298.15\text{ K}) - H^\circ(0\text{ K})](\text{CH}_3\text{CO}) = 12.385\text{ kJ mol}^{-1}$  as given below, and the CODATA<sup>26</sup> recommended values  $\Delta_f H^\circ_{298}(\text{CO}) = -110.53 \pm 0.17\text{ kJ mol}^{-1}$ ,  $[H^\circ(298.15\text{ K}) - H^\circ(0\text{ K})](\text{CO}) = 8.671 \pm 0.01\text{ kJ mol}^{-1}$ ,  $\Delta_f H^\circ_{298}(\text{H}) = 217.998 \pm 0.006\text{ kJ mol}^{-1}$ ,  $[H^\circ(298.15\text{ K}) - H^\circ(0\text{ K})](\text{H}) = 6.197 \pm 0.001\text{ kJ mol}^{-1}$ ,  $[H^\circ(298.15\text{ K}) - H^\circ(0\text{ K})](\text{C, graphite}) = 1.050 \pm 0.020\text{ kJ mol}^{-1}$ ,  $[H^\circ(298.15\text{ K}) - H^\circ(0\text{ K})](\text{H}_2) = 8.468 \pm 0.001\text{ kJ mol}^{-1}$ , and  $[H^\circ(298.15\text{ K}) - H^\circ(0\text{ K})](\text{O}_2) = 8.680 \pm 0.002\text{ kJ mol}^{-1}$ .

Geometry (distance in Å, angles in degrees)<sup>(2a)</sup>

Z matrix						Cartesian coordinates		
						x	y	z
C					C	0.000 000	-0.427 312	-0.137 547
O	1	1.1890			O	0.000 000	0.179 076	-1.160 270
C	1	1.5172	2	127.868	C	0.000 000	0.127 886	1.274 266
H	3	1.0980	1	111.502	2	0	1.224 881	1.274 936
H	3	1.0950	1	108.796	2	121.766	-0.250 864	1.802 321
H	1	1.0950	1	108.796	2	-121.766	-0.250 864	1.802 321

Moments of inertia in the electronic ground state<sup>(2b)</sup>

$$I_A = 9.512 \times 10^{-47}\text{ kg m}^2 \quad I_B = 88.811 \times 10^{-47}\text{ kg m}^2 \quad I_C = 88.028 \times 10^{-47}\text{ kg m}^2$$

$$I_r = 2.662 \times 10^{-47}\text{ kg m}^2 \quad (V_3 = 92\text{ cm}^{-1}, \sigma_{\text{int}} = 3)$$

Vibrational wave numbers in the electronic ground state  $\nu_i(\text{cm}^{-1})$ <sup>(2c)</sup>

2904( <i>a'</i> )	2826( <i>a'</i> )	1886( <i>a'</i> )
1402( <i>a'</i> )	1325( <i>a'</i> )	1025( <i>a'</i> )
817( <i>a'</i> )	454( <i>a'</i> )	2903( <i>a''</i> )
1405( <i>a''</i> )	925( <i>a''</i> )	94( <i>a''</i> , torsion)

Heat Capacity  $C_p^\circ$ , Entropy  $S^\circ$ , and Enthalpy Increment  $[H^\circ(T) - H^\circ(0\text{ K})]$ <sup>(2d),(2e)</sup>

T/K	$C_p^\circ(T)$ ( $\text{JK}^{-1}\text{mol}^{-1}$ )	$S^\circ(T)$ ( $\text{JK}^{-1}\text{mol}^{-1}$ )	$[H^\circ(T) - H^\circ(0\text{ K})]$ ( $\text{kJ mol}^{-1}$ )
150	40.308	236.935	5.716
200	43.076	248.886	7.797
250	46.727	258.876	10.039
298.15	50.785	267.448	12.385
300	50.947	267.762	12.479
350	55.415	275.950	15.138
400	59.882	283.642	18.020
500	68.291	297.925	24.436
600	75.725	311.048	31.646
800	87.813	334.570	48.057
1000	96.873	355.188	66.569
1200	103.619	373.476	86.652
1500	110.665	397.412	118.871
2000	117.510	430.293	176.100
2500	121.214	456.951	235.868
3000	123.396	479.260	297.065

## 7-Constant NASA Polynomial

ACETYL RADICAL	JUN03 C	2.H	3.O	1.	0.G	200.000	6000.000	43.04462	1
	0.53137165E+01	0.91737793E-02	-0.33220386E-05	0.53947456E-09	-0.32452368E-13				2
	-0.36450414E+04	-0.16757558E+01	0.40358705E+01	0.87729487E-03	0.30710010E-04				3
	-0.39247565E-07	0.15296869E-10	-0.26820738E+04	0.78617682E+01	-0.12388039E+04				4

## 9-Constant NASA Polynomial

ACETYL RADICAL	IUPAC Task Group on Selected Radicals								
3 JUN03 C	2.00H	3.00O	1.00	0.00	0.00	0	43.04462	-10300.000	
50.000	200.0007	-2.0	-1.0	0.0	1.0	2.0	3.0	4.0	0.0
-0.289526090D+03	-0.224742331D+02	0.605096002D+01	-0.271517644D-01	0.215987228D-03					
-0.680810164D-06	0.929713833D-09	0.000000000D+00	-0.270326257D+04	0.312464303D+00					
200.000	1000.0007	-2.0	-1.0	0.0	1.0	2.0	3.0	4.0	0.0
-0.832517467D+05	0.166349507D+04	-0.821828123D+01	0.440865769D-01	-0.466819786D-04					
0.281559250D-07	-0.727271377D-11	0.000000000D+00	-0.101449608D+05	0.727981860D+02					
1000.000	6000.0007	-2.0	-1.0	0.0	1.0	2.0	3.0	4.0	0.0
0.241707944D+07	-0.110326222D+05	0.221114619D+02	-0.223777883D-02	0.434799315D-06					
-0.450988885D-10	0.193091426D-14	0.000000000D+00	0.627792109D+05	-0.117810562D+03					

### Comments on Molecular Data, Heat Capacity, Entropy and Enthalpy Increment

(2a) The structural data (Z-matrix and Cartesian coordinates) are the results of G3MP2B3 *ab initio* computations.<sup>14</sup>

(2b) The listed moments of inertia correspond to the rotational constants  $A_e = 2.943 \text{ cm}^{-1}$ ,  $B_e = 0.334 \text{ cm}^{-1}$ , and  $C_e = 0.318 \text{ cm}^{-1}$ , and the rotational constant of the internal rotation,  $B_{\text{int}} = 10.516 \text{ cm}^{-1}$ , as used by Niiranen *et al.*,<sup>5</sup> who based it on *ab initio* calculations reported by Nimlos *et al.*<sup>4</sup> [see (1d) and (1e) above].

(2c) The vibrational wave numbers are those adopted by Niiranen *et al.*,<sup>5</sup> and are based on Hartree–Fock calculations with 6-311+G\*\* basis set reported by Nimlos *et al.*<sup>4</sup> [see (1d) and (1e) above]. The indicated frequencies are scaled using the scaling factor of 0.89. The last frequency is a pseudovibration corresponding to the CH<sub>3</sub> internal rotor.

(2d) The heat capacities, entropies and enthalpy increments were calculated using the rigid rotor-harmonic oscillator approach, in a manner analogous to that reported by Niiranen *et al.*<sup>5</sup> [see (1e) above]. The molecular constants of CH<sub>3</sub>CO are those listed above. The torsion motion is treated as a hindered rotor with a barrier of  $92.0 \text{ cm}^{-1}$  (as estimated by Niiranen *et al.*<sup>5</sup> from the torsional frequency  $94 \text{ cm}^{-1}$ ), and assumed to be a three-cycle sinusoidal potential with  $\sigma_{\text{int}} = 3$ . Although based on the same molecular constants, the values obtained by Niiranen *et al.*<sup>5</sup> are slightly different because they estimated the contribution of the internal rotor by using the tabulated values of Pitzer and Gwinn.<sup>37</sup>

(2e) The standard heat capacity, entropy, and enthalpy increment values reported in the *Thermochemical Database for Combustion*<sup>23</sup> are  $C_p^\circ(298.15 \text{ K}) = 50.784 \text{ J K}^{-1} \text{ mol}^{-1}$ ,  $S^\circ(298.15 \text{ K}) = 267.449 \text{ J K}^{-1} \text{ mol}^{-1}$ , those obtained from G3MP2B3 computations<sup>14</sup> are  $C_p^\circ(298.15 \text{ K}) = 54.70 \text{ J K}^{-1} \text{ mol}^{-1}$ ,  $S^\circ(298.15 \text{ K}) = 269.94 \text{ J K}^{-1} \text{ mol}^{-1}$ ,  $H^\circ(298.15 \text{ K}) - H^\circ(0 \text{ K}) = 13.01 \text{ kJ mol}^{-1}$ , and those reported by Niiranen *et al.*<sup>5</sup> are  $C_p^\circ(298.15 \text{ K}) = 50.769 \text{ J K}^{-1} \text{ mol}^{-1}$ ,  $S^\circ(298.15 \text{ K}) = 267.46 \text{ J mol}^{-1} \text{ K}^{-1}$ ,  $H^\circ(298.15 \text{ K}) - H^\circ(0 \text{ K}) = 12.388 \text{ kJ mol}^{-1}$ .

### References

- K. W. Watkins and W. W. Word, *Int. J. Chem. Kinet.* **6**, 855 (1974).
- J. L. Holmes and F. P. Lossing, *Int. J. Mass. Spectrom.* **58**, 113 (1984).
- W. Tsang, *Int. J. Chem. Kinet.* **16**, 1543 (1984).
- M. R. Nimlos, J. A. Soderquist, and G. B. Ellison, *J. Am. Chem. Soc.* **111**, 7675 (1989).
- J. T. Niiranen, D. Gutman, and L. N. Krasnoperov, *J. Phys. Chem.* **96**, 5881 (1992).
- S. H. Mousavipour and P. D. Pacey, *J. Phys. Chem.* **100**, 3573 (1996).
- J. S. Francisco and N. J. Abersold, *Chem. Phys. Lett.* **187**, 354 (1991).
- C. W. Bauschlicher, Jr., *J. Phys. Chem.* **98**, 2564 (1994).
- M. R. Zachariah, P. R. Westmoreland, D. R. Burgess, Jr., W. Tsang, and C. F. Melius, *J. Phys. Chem.* **100**, 8737 (1996); see also D. R. F. Burgess, Jr., M. R. Zachariah, W. Tsang, and P. R. Westmoreland, *Prog. Energy Combust. Sci.* **21**, 453 (1995).
- L. A. Curtiss, K. Raghavachari, P. C. Redfern, and B. S. Stefanov, *J. Chem. Phys.* **108**, 692 (1998).
- L. A. Curtiss, K. Raghavachari, P. C. Redfern, V. Rassolov, and J. A. Pople, *J. Chem. Phys.* **109**, 7764 (1998).
- B. Viskolcz and T. Bérces, *Phys. Chem. Chem. Phys.* **2**, 5430 (2000).
- S. Parthiban and J. M. L. Martin, *J. Chem. Phys.* **114**, 6014 (2001).
- R. Janoschek and M. J. Rossi, *Int. J. Chem. Kinet.* **34**, 550 (2002).
- D. D. Wagman, W. E. Evans, V. B. Parker, R. H. Schumm, I. Halow, S. M. Bailey, K. L. Churney, and R. L. Nuttall, *The NBS Tables of Chemical Thermodynamic Properties*, *J. Phys. Chem. Ref. Data* **11**, Suppl. 2 (1982).
- D. F. McMillen and D. M. Golden, *Ann. Rev. Phys. Chem.* **33**, 493 (1982).
- J. Berkowitz, G. B. Ellison, and D. Gutman, *J. Phys. Chem.* **98**, 2744 (1994).
- W. Tsang, *Heats of Formation of Organic Free Radicals by Kinetic Methods*, in *Energetics of Organic Free Radicals*, edited by J. A. M. Simoes, A. Greenberg, and J. F. Liebman, Structure, Energetics and Reactivity in Chemistry (SEARCH) Series (Chapman and Hall, London, 1996).
- J. C. Traeger and B. M. Kompe, *Thermochemical Data for Free Radicals from Studies of Ions*, in *Energetics of Organic Free Radicals*, edited by J. A. M. Simoes, A. Greenberg, and J. F. Liebman, Structure, Energetics and Reactivity in Chemistry (SEARCH) Series (Chapman and Hall, London, 1996).
- Computational Chemistry Comparison and Benchmark DataBase (CCCBDB), NIST (1999); see <http://srdata.nist.gov/cccbdb/>
- R. Atkinson, D. L. Baulch, R. A. Cox, R. F. Hampson, Jr., J. A. Kerr, M. J. Rossi, and J. Troe, *J. Phys. Chem. Ref. Data* **29**, 167 (2000).
- J. A. Kerr and D. W. Stocker, *Strengths of Chemical Bonds*, in *CRC Handbook of Chemistry and Physics*, 81st ed. (CRC, Boca Raton, FL, 2000–2001).
- A. Burcat, TAE Report No.867, Technion, Haifa, see also <ftp://ftp.technion.ac.il/pub/supported/aetdd/thermodynamics>
- S. P. Sander, R. R. Friedl, D. M. Golden, M. J. Kurylo, R. E. Huie, V. L.

- Orkin, G. K. Moortgat, A. R. Ravishankara, C. E. Kolb, M. J. Molina, and B. J. Finlayson-Pitts, JPL Publication 02-25, NASA and JPL, February 1, 2003.
- <sup>25</sup> H. Y. Afeefy, J. F. Liebman, and S. E. Stein, *Neutral Thermochemical Data in NIST Chemistry WebBook*, NIST Standard Reference Database Number 69, edited by P. J. Linstrom and W. G. Mallard (NIST, Gaithersburg, MD, 2003), (<http://webbook.nist.gov/>)
- <sup>26</sup> J. D. Cox, D. D. Wagman, and V. A. Medvedev, *CODATA Key Values for Thermodynamics* (Hemisphere, New York, 1989), see also (<http://www.codata.org/codata/databases/key1.html>)
- <sup>27</sup> J. C. Traeger and R. G. McLoughlin, *J. Am. Chem. Soc.* **103**, 3647 (1981).
- <sup>28</sup> R. Yamdagni and P. Kebarle, *J. Am. Chem. Soc.* **98**, 1320 (1976).
- <sup>29</sup> F. P. Lossing, *J. Am. Chem. Soc.* **99**, 7526 (1977).
- <sup>30</sup> F. P. Lossing and A. Maccoll, *Can. J. Chem.* **54**, 990 (1976).
- <sup>31</sup> J. C. Traeger, R. G. McLoughlin, and A. J. C. Nicholson, *J. Am. Chem. Soc.* **104**, 5312 (1982).
- <sup>32</sup> J. B. Pedley and J. Rylance, *Sussex—N.P.L. Computer Analyzed Thermochemical Data: Organic and Organometallic Compounds* (University of Sussex Press, Sussex, 1977).
- <sup>33</sup> W. Tsang, in *Shock Waves in Chemistry*, edited by A. Lifshitz (Dekker, New York, 1981), p.59.
- <sup>34</sup> D. R. Stull, E. G. Westrum, and G. C. Sinke, *The Chemical Thermodynamics of Organic Compounds* (Wiley, New York, 1969).
- <sup>35</sup> C. H. DePuy, V. M. Bierbaum, R. Damrauer, and J. A. Soderquist, *J. Am. Chem. Soc.* **107**, 3385 (1985).
- <sup>36</sup> J. M. Nicovich, C. J. Shackelford, and P. H. Wine, *J. Photochem. Photobiol. A* **51**, 141 (1990).
- <sup>37</sup> K. S. Pitzer and W. D. Gwinn, *J. Chem. Phys.* **10**, 428 (1942).
- <sup>38</sup> A. Burcat, in *Combustion Chemistry*, edited by W. C. Gardiner (Springer, New York, 1984), Chap. 8.
- <sup>39</sup> R. Atkinson, D. L. Baulch, R. A. Cox, R. F. Hampson, Jr., J. A. Kerr, and J. Troe, *J. Phys. Chem. Ref. Data* **18**, 881 (1989).
- <sup>40</sup> J. Chao, K. R. Hall, K. N. Marsh, and R. C. Wilhoit, *J. Phys. Chem. Ref. Data* **15**, 1369 (1986).
- <sup>41</sup> M. W. Chase, Jr., C. A. Davies, J. R. Downey, Jr., D. J. Frurip, R. A. McDonald, and A. N. Syverud, *JANAF Thermochemical Tables*, 3rd ed., *J. Phys. Chem. Ref. Data* **14**, Suppl. 1 (1985).
- <sup>42</sup> J. Troe, *J. Phys. Chem.* **83**, 114 (1979).
- <sup>43</sup> L. V. Gurvich, V. S. Iorish, V. S. Yungman, and O. V. Dorofeeva, *Thermodynamic Properties as a Function of Temperature in Handbook of Chemistry and Physics*, 75th ed., edited by D. R. Lide (1995), pp. 5–55; this table lists as references JANAF Tables 3rd ed. and L. V. Gurvich, I. V. Veys, and C. B. Alcock, *Thermodynamic Properties of Individual Substances*, 4th ed. (Hemisphere, New York, 1989–1991), Vols. 1 and 2.
- <sup>44</sup> J. Ernst and K. Spindler, *Ber. Bunsenges. Phys. Chem.* **79**, 1163 (1975); J. Ernst and K. Spindler, *ibid.* **80**, 645 (1976).
- <sup>45</sup> P. Warneck, *Z. Naturforsch.* **26a**, 2047 (1971); **29**, 350 (1974).
- <sup>46</sup> J. S. Francisco and Y. Zhao, *J. Chem. Phys.* **93**, 9203 (1990).
- <sup>47</sup> J. N. Nicovich, K. D. Kreutter, and P. H. Wine, *J. Chem. Phys.* **92**, 3539 (1990).
- <sup>48</sup> A. S. Rodgers, J. Chao, R. C. Wilhoit, and B. S. Zwolinski, *J. Phys. Chem. Ref. Data* **3**, 117 (1974).
- <sup>49</sup> W. A. Chupka, *J. Chem. Phys.* **48**, 2337 (1968).
- <sup>50</sup> O. Dobis and S. W. Benson, *Int. J. Chem. Kinet.* **19**, 691 (1987).
- <sup>51</sup> L. A. Curtiss, P. C. Redfern, K. Raghavachari, V. Rassolov, and J. A. Pople, *J. Chem. Phys.* **110**, 4703 (1999).
- <sup>52</sup> L. A. Curtiss, K. Raghavachari, P. C. Redfern, and J. A. Pople, *J. Chem. Phys.* **106**, 1063 (1997).
- <sup>53</sup> H.-Q. Zhao, Y.-S. Cheung, C.-L. Liao, C.-X. Liao, and C. Y. Ng, *J. Chem. Phys.* **107**, 7230 (1997).
- <sup>54</sup> J. D. Cox and G. Pilcher, *Thermochemistry of Organic and Organometallic Compounds* (Academic, London, 1970).
- <sup>55</sup> A. G. Baboul, L. A. Curtiss, P. C. Redfern, and K. Raghavachari, *J. Chem. Phys.* **110**, 7650 (1999).
- <sup>56</sup> J. C. Traeger, R. G. McLoughlin, and A. J. C. Nicholson, *J. Am. Chem. Soc.* **104**, 5318 (1982).
- <sup>57</sup> M. A. Dolliver, T. J. Gresham, G. B. Kistiakowsky, E. A. Smith, and W. E. Vaughan, *J. Am. Chem. Soc.* **60**, 440 (1938).

## 7.3. Oxygen-Centered Radicals

## 7.3.1. OH Radical

## 7.3.1. Hydroxyl radical

3352-57-6

OH ( ${}^2\Pi_{3/2}$ )	$C_{\infty v}(\sigma=1)$
$\Delta_f H^\circ(298.15\text{ K}) = 37.3 \pm 0.3\text{ kJ mol}^{-1}$	$\Delta_f H^\circ(0\text{ K}) = 37.1 \pm 0.3\text{ kJ mol}^{-1}$
$C_p^\circ(298.15\text{ K}) = 29.886\text{ J K}^{-1}\text{ mol}^{-1}$	$H^\circ(298.15\text{ K}) - H^\circ(0\text{ K}) = 8.813\text{ kJ mol}^{-1}$
$S^\circ(298.15\text{ K}) = 183.737\text{ J K}^{-1}\text{ mol}^{-1}$	$p^\circ = 100\,000\text{ Pa (1 bar)}$

## Literature Data for the Enthalpy of Formation at 298.15 K

$\Delta_f H^\circ/\text{kJ mol}^{-1}$	Authors and Reference	Method <sup>a</sup>	Comments
<b>Measurements</b>			
$39.0^b \pm 1.2^c$	Barrow (1956) <sup>1</sup>	SPEC	(1a)
$39.35^b \pm 0.20^c$	Carlone and Dalby (1969) <sup>2</sup>	SPEC	(1b)
$37.2^b \pm 0.8^c$	McCulloh (1973) <sup>3</sup>	PIMS-PIC	(1c)
$37.2 \pm 0.4$	Ruscic <i>et al.</i> (2001) <sup>4</sup>	PIMS-PIC	(1d)
$37.56^b \pm 0.07^c$	Harich <i>et al.</i> (2000) <sup>5</sup>	SPEC	(1e)
$37.29 \pm 0.29$	Ruscic <i>et al.</i> (2002) <sup>6</sup>	PIMS-PIC	(1f)
$37.3 \pm 0.7$	Herbon <i>et al.</i> (2002) <sup>7</sup>	KE	(1g)
<b>Computations</b>			
$39.7 \pm 8.9^c$	Melius (1990) <sup>8</sup>	BAC-MP4	(1h)
$37.7 \pm 13^c$	Curtiss <i>et al.</i> (1998) <sup>9</sup>	CBS-Q	(1i)
$35.1 \pm 7.9^c$	Curtiss <i>et al.</i> (1998) <sup>10</sup>	G3	(1j)
$37.5 \pm 1.9^c$	Parthiban and Martin (2001) <sup>11</sup>	W2	(1k)
$37.4 \pm 0.7$	Ruscic <i>et al.</i> (2001) <sup>4</sup>	CCSD(T)	(1l)
$37.3 \pm 0.7$	Ruscic <i>et al.</i> (2002) <sup>6</sup>	CCSD(T)	(1m)
$33.9 \pm 7.8^c$	Janoschek and Rossi (2002) <sup>12</sup>	G3MP2B3	(1n)
<b>Reviews and Evaluations</b>			
38.95	NBS (1982) <sup>13</sup>	TT-U	(1o)
39.3	McMillen and Golden (1982) <sup>14</sup>	CDE	(1p)
$39.0 \pm 1.2$	JANAF (1985) <sup>15</sup>	CDE	(1q)
$39.35 \pm 0.21$	Gurvich <i>et al.</i> (1989) <sup>16</sup>	CDE	(1r)
$39.3 \pm 0.2$	Berkowitz <i>et al.</i> (1994) <sup>17</sup>	CDE	(1s)
$39.35 \pm 0.21$	NIST CCCBDB (1999) <sup>18</sup>	TT-A	(1t)
39.0	CRC HCP (2001) <sup>19</sup>	TT-U	(1u)
39.3	Kerr and Stocker (2001) <sup>20</sup>	TT-A	(1v)
$39.3 \pm 2.1$	Atkinson <i>et al.</i> (2000) <sup>21</sup>	TT-A	(1w)
39.3	Burcat (2001) <sup>22</sup>	TT-A	(1x)
$37.5^b \pm 1.6^c$	Joens (2001) <sup>23</sup>	CDE	(1y)
$37.29 \pm 0.29$	Ruscic <i>et al.</i> (2002) <sup>6</sup>	CDE	(1z)
$37.20 \pm 0.38$	Sander <i>et al.</i> (2003) <sup>24</sup>	TT-A	(1aa)
38.99	NIST WebBook (2003) <sup>25</sup>	TT-A	(1bb)

<sup>a</sup>PIMS-PIC: positive ion cycle based on combining photoionization measurements of fragment appearance energy ( $E_{\text{ap}}$ ) from a stable molecule with ionization energy ( $E_i$ ) of the radical; KE: kinetic equilibrium study; SPEC: spectroscopic study; CDE: critical data evaluation; TT-U: unannotated tabulation of thermodynamic data; and TT-A: annotated tabulation of thermodynamic data.

<sup>b</sup>The quoted value was either not given explicitly by the author(s) or it was recalculated using auxiliary thermochemical values that differ from those used by the original authors; see individual comments for additional details.

<sup>c</sup>The uncertainty was either not given explicitly by the original author(s) or it has been modified; see individual comments for further explanations.

**Comments on the Enthalpies of Formation**

(1a) Spectroscopic determination of  $D_0(\text{OH})$  based on Birge–Sponer extrapolation of observed vibrational levels of the  $\tilde{A}^2\Sigma^+$  state of OH. The actual extrapolated value was  $35\,427\text{ cm}^{-1}$ , which, in order to compensate for a suspected underestimate, was increased in the final analysis to  $35\,450 \pm 100\text{ cm}^{-1}$  by the author. This produces the listed value for  $\Delta_f H^\circ_{298}(\text{OH})$  when combined with the CODATA<sup>26</sup> recommended values  $\Delta_f H^\circ_{298}(\text{H}) = 217.998 \pm 0.006\text{ kJ mol}^{-1}$ ,  $[H^\circ(298.15\text{ K}) - H^\circ(0\text{ K})](\text{H}) = 6.197 \pm 0.001\text{ kJ mol}^{-1}$ ,

$\Delta_f H^\circ_{298}(\text{O}) = 249.18 \pm 0.10\text{ kJ mol}^{-1}$ , and  $[H^\circ(298.15\text{ K}) - H^\circ(0\text{ K})](\text{O}) = 6.725 \pm 0.001\text{ kJ mol}^{-1}$ , together with  $[H^\circ(298.15\text{ K}) - H^\circ(0\text{ K})](\text{OH}) = 8.813\text{ kJ mol}^{-1}$  from Gurvich *et al.*<sup>16</sup>

(1b) Spectroscopic determination of  $D_0(\text{OH}) = 35\,420 \pm 15\text{ cm}^{-1}$ , based on a relatively short Birge–Sponer extrapolation ( $272\text{ cm}^{-1}$  beyond the last observed vibrational level) of observed vibrational levels of the  $\tilde{A}^2\Sigma^+$  state of OH. The authors have improved on the data obtained earlier by Barrow<sup>1</sup> and expanded the number of observed levels.

The quoted dissociation energy corresponds to  $D_0(\text{OH}, \tilde{A}^2\Sigma^+) = 18\,47 \pm 15 \text{ cm}^{-1}$ , which refers to the  $\text{O}(^1D_2) + \text{H}(^2S)$  dissociation asymptote. The desired dissociation energy of ground state  $\tilde{X}^2\Pi_{3/2}, J=3/2, v=0$  of OH producing  $\text{H}(^2S) + \text{O}(^3P_2)$  can be obtained by adding the energy<sup>27,28</sup> of the  $P_1(1)$  transition of  $32\,440.6 \text{ cm}^{-1}$  to  $D_0(\text{OH}, \tilde{A}^2\Sigma^+)$  and subtracting the term value<sup>29</sup> for  $\text{O}(^1D_2)$  of  $15\,867.7 \text{ cm}^{-1}$ . An even shorter extrapolation ( $114 \text{ cm}^{-1}$  beyond the last observed level) leads to an apparently congruent value for the dissociation energy of OD. The  $\Delta_f H^\circ_{298}(\text{OH})$  value listed in the table is obtained by using auxiliary thermochemical values as given in (1a) above.

(1c) Photoionization mass spectrometric study of water. McCulloh performed a very detailed photoionization study on  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$ . For  $\text{H}_2\text{O}$  he reported the 0 K fragmentation onset of  $18.115 \pm 0.008 \text{ eV}$ . McCulloh originally used this threshold and the bond dissociation energy of water that results from the 2nd ed. of JANAF Tables<sup>30</sup> to derive  $E_{i,\text{ad}}(\text{OH})$ , which was the major unknown at the time. However, with the best currently available value<sup>31</sup>  $E_{i,\text{ad}}(\text{OH}) = 104\,989 \pm 2 \text{ cm}^{-1} = 13.016\,98 \pm 0.000\,25 \text{ eV}$ , the appearance threshold results in  $D_0(\text{H}-\text{OH}) = 491.88 \pm 0.77 \text{ kJ mol}^{-1}$ . This implies  $\Delta_f H^\circ_0(\text{OH}) = 36.93 \pm 0.77 \text{ kJ mol}^{-1}$  when combined with auxiliary thermochemical values as given in (1a) above and the CODATA<sup>26</sup> recommended values  $\Delta_f H^\circ_{298}(\text{H}_2\text{O}) = -241.826 \pm 0.040 \text{ kJ mol}^{-1}$  and  $[H^\circ(298.15 \text{ K}) - H^\circ(0 \text{ K})](\text{H}_2\text{O}) = 9.905 \pm 0.005 \text{ kJ mol}^{-1}$ .

(1d) The authors have addressed the inconsistency between  $D_0(\text{OH})$  from spectroscopic considerations [see (1b) above] and  $D_0(\text{H}-\text{OH})$  obtained from photoionization results [see (1c) above]. The sum of these two bond energies exceeds the accepted atomization energy of water<sup>26</sup> by  $\sim 2 \text{ kJ mol}^{-1}$ . *Inter alia*, the authors present a new particularly careful photoionization study of the threshold for  $\text{OH}^+$  fragment formation from water, with special consideration to effects that could potentially lead to an early threshold. This results in a fitted value  $E_{\text{ap},0}(\text{OH}^+/\text{H}_2\text{O}) = 18.115_3 \pm 0.003_5 \text{ eV}$ , in excellent agreement with the earlier study of McCulloh.<sup>3</sup> Together with the ZEKE value<sup>31</sup>  $E_{i,\text{ad}}(\text{OH}) = 13.0170 \pm 0.0003 \text{ eV}$ , the fitted fragment appearance energy leads to  $D_0(\text{H}-\text{OH}) = 491.9 \pm 0.3 \text{ kJ mol}^{-1}$ , and hence the listed value. The study also reports a brief analysis of why the spectroscopic result<sup>2</sup> [see (1b) above] is probably in error, as well as high level *ab initio* calculations [see (1l) below] that support the claim.

(1e) Photodissociation measurements on water using the Rydberg tagging technique. The reported value is  $D_0(\text{H}-\text{OH}) = 41\,151 \pm 5 \text{ cm}^{-1} = 492.28 \pm 0.06 \text{ kJ mol}^{-1}$ . This implies  $\Delta_f H^\circ_0(\text{OH}) = 36.56 \pm 0.07 \text{ kJ mol}^{-1}$  when combined with auxiliary thermochemical values as given in (1a) and (1c) above.

(1f) A followup paper to the one discussed in (1d) above. The paper contains additional photoionization measurements, additional high level calculations [see (1m) below], as well as an analysis demonstrating that the Birge–Sponer extrapolation

results [see (1b) above] seriously underestimate  $D_0(\text{OH})$ . From a refined fit of the photoionization mass spectrometric threshold for the appearance of the  $\text{OH}^+$  fragment from water<sup>4</sup> the authors obtain  $E_{\text{ap},0}(\text{OH}^+/\text{H}_2\text{O}) = 146\,116 \pm 28 \text{ cm}^{-1} = 18.116_1 \pm 0.003_5 \text{ eV}$ . In addition, two new photoionization measurements are presented: PFI-PE resulting in  $E_{\text{ap},0}(\text{OH}^+/\text{H}_2\text{O}) = 146\,119 \pm 16 \text{ cm}^{-1} = 18.116_5 \pm 0.002_0 \text{ eV}$ , and PFI-PEPICO, which produces  $E_{\text{ap},0}(\text{OH}^+/\text{H}_2\text{O}) = 146\,107 \pm 40 \text{ cm}^{-1} = 18.115 \pm 0.005 \text{ eV}$ . From these three determinations and a previous value from McCulloh<sup>3</sup> [see (1c) above], a consensus value of  $E_{\text{ap},0}(\text{OH}^+/\text{H}_2\text{O}) = 146\,117 \pm 24 \text{ cm}^{-1} = 18.116_3 \pm 0.003_0 \text{ eV}$  is obtained. Together with the ZEKE value<sup>31</sup>  $E_{i,\text{ad}}(\text{OH}) = 104\,989 \pm 2 \text{ cm}^{-1} = 13.016\,98 \pm 0.000\,25 \text{ eV}$ , this leads to  $D_0(\text{H}-\text{OH}) = 41\,128 \pm 24 \text{ cm}^{-1} = 429.00 \pm 0.29 \text{ kJ mol}^{-1}$ , corresponding to  $D_0(\text{OH}) = 35\,593 \pm 25 \text{ cm}^{-1} = 425.79 \pm 0.30 \text{ kJ mol}^{-1}$  and  $\Delta_f H^\circ_0(\text{OH}) = 37.04 \pm 0.29 \text{ kJ mol}^{-1}$ .

(1g) A very carefully designed experiment producing measurements of “partial equilibrium” of OH with  $\text{H}_2$  and  $\text{O}_2$  designed to critically test the value of Ruscic *et al.*<sup>4,6</sup> [see (1f) above] using kinetic methods. The data were fitted with an extensive reaction mechanism, but the only fitted parameter was the enthalpy of formation of OH.

(1h) BAC-MP4 *ab initio* computations. The originally quoted uncertainty is  $\pm 4.4 \text{ kJ mol}^{-1}$ , and has been multiplied by factor of 2 to bring it closer to the desired 95% confidence limit.

(1i) CBS-Q value. The reported average absolute deviation of  $1.57 \text{ kcal mol}^{-1}$  was multiplied by 2 to bring it closer to the desired 95% confidence limit. The equivalent CBS-q and CBS-4 enthalpies of formation are  $38.9 \pm 18$  and  $40.2 \pm 26 \text{ kJ mol}^{-1}$ , where the uncertainties have been obtained in an analogous way.

(1j) G3 *ab initio* calculation. The value listed in the table is converted from  $34.0 \text{ kcal mol}^{-1}$ . The uncertainty quoted in the table corresponds approximately to 95% confidence limits, based on twice the average absolute deviation of  $0.94 \text{ kcal mol}^{-1}$  for the enthalpies in the G2/97 test set, which roughly corresponds to one standard deviation. At the G3(MP2) level of theory<sup>33</sup>  $\Delta_f H^\circ_{298}(\text{OH}) = 34.7 \pm 9.9 \text{ kJ mol}^{-1}$ , where the quoted uncertainty has been derived in a similar fashion as for the G3 value. At the G2 level of theory<sup>33</sup>  $\Delta_f H^\circ_{298}(\text{OH}) = 38.1 \pm 13.1 \text{ kJ mol}^{-1}$ .

(1k) W2 *ab initio* calculation. The uncertainty quoted in the table corresponds approximately to 95% confidence limits based on twice the average absolute deviation for the W2 test set of  $0.23 \text{ kcal mol}^{-1}$ , which corresponds roughly to one standard deviation. At the W1 level of theory  $\Delta_f H^\circ_{298}(\text{OH}) = 36.8 \pm 3.1 \text{ kJ mol}^{-1}$ , where the uncertainty has been obtained in an analogous way.

(1l) CCSD(T)/aug-cc-pVnZ calculations,  $n=3, 4, 5, 6$ , extrapolated to CBS, and corrected for core–valence effects, scalar relativistic effects, and incomplete CI. The calculated values were further adjusted using experimental zero-point energies and spin–orbit splittings. The final value and its uncertainty are estimated from the upper limit/lower limit approach through calculated  $D_0(\text{H}-\text{OH})$  and  $D_0(\text{OH})$ . In

addition, the quoted uncertainty was validated by comparing results calculated at the same level for the atomization energy of water and ionization energy of OH to known experimental values.

(1m) CCSD(T)/aug-cc-pVnZ calculations,  $n=4, 5, 6, 7$ , extrapolated to CBS, with additional corrections as those described in (11) above. Compared to (11) above, this set of calculations was improved by including basis sets of 7- $\zeta$  quality and including additional corrections. This further reduces the small uncertainties in the earlier calculation so that the current theoretical uncertainty reflects primarily the variations between various approaches to the CBS extrapolation. The uncertainty that would arise from considerations similar to those described in (11) above would be less than half the quoted uncertainty. The listed value is an average of the enthalpy obtained from the calculated  $D_0(\text{H-OH}) = 491.92 \pm 0.21 \text{ kJ mol}^{-1}$ , which produces  $\Delta_f H^\circ_{298}(\text{OH}) = 37.20 \pm 0.21 \text{ kJ mol}^{-1}$ , and  $D_0(\text{OH}) = 425.62 \pm 0.26 \text{ kJ mol}^{-1}$ , which produces  $\Delta_f H^\circ_{298}(\text{OH}) = 37.45 \pm 0.27 \text{ kJ mol}^{-1}$ .

(1n) G3(MP2)//B3LYP *ab initio* calculations for 32 selected free radicals. The uncertainty given in the table corresponds approximately to 95% confidence limits based on twice the quoted average absolute deviation of  $3.9 \text{ kJ mol}^{-1}$  for the calculated set of radicals, which corresponds roughly to 1 s.d. Note that the average absolute deviation for all enthalpies in the G2/97 test set using the same method is very slightly larger:<sup>34</sup>  $4.7 \text{ kJ mol}^{-1}$  [see also (1j) above].

(1o) Critical data evaluation, but does not provide a pedigree of the selected value nor does it quote an uncertainty, although the value seems to be quite close to that adopted by JANAF<sup>15</sup> [see (1j) above].

(1p) Recommended value from extensive evaluation of data (mainly kinetic determinations) published till 1981. The quoted source for the enthalpy of OH is the 2nd ed. of JANAF.<sup>30</sup> The value in the 2nd ed. is nominally based on the determination by Barrow<sup>1</sup> [see (1a) above] that was also used in the 3rd ed. of JANAF<sup>15</sup> [see (1q) below], but for some reason the adopted  $D_0(\text{OH})$  was  $35\,440 \pm 100 \text{ cm}^{-1}$ . In addition, the transformation from the 0 K value to the 298.15 K value is erroneous in all editions of JANAF, and hence the nominal similarity to the value obtained from more accurate spectroscopic considerations<sup>2,16</sup> [see (1b) above and (1r) below].

(1q) Extensive compilation of thermodynamic data. The OH properties have been last revised in June 1977. The value is supposedly based on Barrow<sup>1</sup> [see (1a) above]. The discussion explicitly states: "A value of  $D_0^\circ(\text{OH}) = 35\,450 \pm 100 \text{ cm}^{-1} = 101.356 \pm 0.29 \text{ kcal mol}^{-1}$  was adopted... one obtains  $\Delta_f H^\circ(\text{OH}, \text{g}, 0 \text{ K}) = 9.261 \pm 0.29 \text{ kcal mol}$ , which is in good agreement with the last JANAF selection," namely with  $\Delta_f H^\circ_0(\text{OH}) = 9.29 \pm 0.3 \text{ kcal mol}^{-1}$  ( $= 38.85 \pm 1.21 \text{ kJ mol}^{-1}$  from the 2nd ed.).<sup>30</sup> The selected value for the 0 K enthalpy of hydroxyl of  $9.261 \pm 0.29 \text{ kcal mol}$  corresponds to  $38.755 \pm 1.21 \text{ kJ mol}^{-1}$ . Inexplicably, the actual value listed on top of their OH page and used to obtain other

tabulated thermodynamic functions is different:  $\Delta_f H^\circ_0(\text{OH}) = 38.390 \pm 1.21 \text{ kJ mol}^{-1}$ . Since this corresponds very closely to  $D_0(\text{OH}) = 35\,480 \pm 100 \text{ cm}^{-1}$ , it is not clear whether the discrepancy is an inadvertent mistake or the authors had some undisclosed reasons to additionally increase Barrow's estimated  $D_0(\text{OH})$  by  $30 \text{ cm}^{-1}$ . The OH data in JANAF is afflicted by a number of additional inaccuracies. The most serious is an incorrect treatment of the degeneracy and multiplicity of the ground electronic state of OH, resulting in large errors in the calculated heat capacity and enthalpy increments. Among others, this results in an erroneous transformation from the 0 K enthalpy to the listed 298.15 K enthalpy of  $38.987 \pm 1.21 \text{ kJ mol}^{-1}$ . Based on the value of  $\Delta_f H^\circ_0(\text{OH})$  listed at the top of their page, the resulting 298.15 K value should have been  $38.629 \pm 1.21 \text{ kJ mol}^{-1}$ , while from the 0 K enthalpy explicitly mentioned in the discussion, the resulting 298.15 K value should have been  $38.994 \pm 1.21 \text{ kJ mol}^{-1}$ . The OH properties have not been revised in the new edition.<sup>35</sup>

(1r) Extensive compilation of thermodynamic data. The value is based entirely on the spectroscopic determination of Carlone and Dalby<sup>2</sup> [see (1b) above], although other, less precise measurements have been also considered. The value is unchanged from the previous (Russian) edition.<sup>36</sup>

(1s) Critical data evaluation of R-H bond dissociation energies based on three methods: kinetic determinations, positive ion cycle determinations from photoelectron/photoionization measurements and negative ion cycle determinations from photoelectron measurements of negative ions combined with gas phase acidities. The recommended value is based on the selection of Gurvich *et al.*<sup>16</sup> [see (1r) above] and hence Carlone and Dalby<sup>2</sup> [see (1b) above]. However, the bond dissociation energy of water that results from the  $\text{OH}^+/\text{H}_2\text{O}$  appearance energy of McCulloh<sup>3</sup> and the adiabatic ionization energy of OH of Wiedman *et al.*<sup>31</sup> [see (1c) above] is listed in their table of photoionization results. In one of the footnotes, the authors point out that for reasons that are not clear, the positive ion cycle produces a  $D_0(\text{H-OH})$  that is lower by  $\sim 2 \text{ kJ mol}^{-1}$ .

(1t) The compilation lists theoretical results at various levels of theory, but also makes a reference to one experimental benchmark. The quoted experimental benchmark value is from Gurvich *et al.*<sup>16</sup> [see (1r) above].

(1u) The tabulation gives a list of compilations as sources, but no specific references for individual species. However, the value appears to correspond to that adopted by NBS Tables<sup>13</sup> [see (1o) above] and JANAF<sup>15</sup> Tables [see (1q) above].

(1v) The tabulation selects the value of McMillen and Golden<sup>14</sup> [see (1p) above], which cites the superseded value from old (2nd) ed. of JANAF.<sup>30</sup> It should be noted that the similarity to the value given in Gurvich *et al.*<sup>16</sup> [see (1b) and (1r) above] is accidental, and arises from erroneous transfor-

mation from the 0 K value to the 298.15 K value in JANAF<sup>30</sup> [see also (1q) above].

(1w) Critical evaluation of atmospherically relevant kinetic data. Their table of enthalpy data lists Kerr and Stocker<sup>20</sup> [see (1v) above] as their source of  $\Delta_f H^\circ_{298}(\text{OH})$ . The quoted uncertainty should have perhaps been 1.2 kJ mol<sup>-1</sup>.

(1x) Thermochemical database for combustion. Burcat quotes Gurvich *et al.*<sup>16</sup> as a source of  $\Delta_f H^\circ_{298}(\text{OH})$ .

(1y) Evaluation of available data, intended to lend additional support and an improvement on the downward revision of  $\Delta_f H^\circ(\text{OH})$  initially reported by Ruscic *et al.*<sup>4</sup> [see (1d) above]. The author utilizes  $D_0(\text{H-OH})$  of Harich *et al.*<sup>5</sup> [see (1e) above] and  $D_0(\text{HO-OH}) = 17\,051.8 \pm 3.4 \text{ cm}^{-1}$  of Luo *et al.*<sup>37</sup> to derive  $\Delta_f H^\circ(\text{OH})$  with an improved uncertainty. From  $D_0(\text{H-OH})$  and the enthalpy of atomization of water from the JANAF Tables,<sup>35</sup>  $D_0(\text{OH}) = 35\,579 \pm 11 \text{ cm}^{-1}$  is obtained. From  $D_0(\text{HO-OH})$  the author obtains  $D_0(\text{OH}) = 35\,589 \pm 12 \text{ cm}^{-1}$ , based on  $\Delta_f H^\circ_0(\text{H}_2\text{O}_2) = -129.808 (\pm 0.2) \text{ kJ mol}^{-1}$  (where the enthalpy is from the JANAF Tables,<sup>35,15</sup> and the uncertainty is derived by the author). By combining the two bond dissociation energies of OH, which would appear to differ by no more than 10 cm<sup>-1</sup>, the author derives  $D_0(\text{OH}) = 35\,584 \pm 10 \text{ cm}^{-1}$ , and hence  $\Delta_f H^\circ(\text{OH}) = 37.14 \pm 0.12 \text{ kJ mol}^{-1}$ . Unfortunately, this derivation has several problems. The value for  $D_0(\text{H-OH})$  of Harich *et al.*<sup>5</sup> has been misquoted by the author by 10 cm<sup>-1</sup>. In addition, the use of  $D_0(\text{HO-OH})$  involves  $\Delta_f H^\circ(\text{H}_2\text{O}_2)$ , which is significantly less firmly established than the enthalpy of formation of water. The  $\Delta_f H^\circ_{298}(\text{H}_2\text{O}_2)$  values in the JANAF Tables<sup>35,15</sup> ( $-136.106 \text{ kJ mol}^{-1}$ , uncertainty not given explicitly) and in Gurvich *et al.*<sup>16</sup> ( $-135.880 \pm 0.220 \text{ kJ mol}^{-1}$ ) differ, where the latter value seems to be more carefully chosen. In addition, the value  $\Delta_f H^\circ_0(\text{H}_2\text{O}_2)$  in the JANAF Tables<sup>35,15</sup> is derived using an inaccurate conversion from  $\Delta_f H^\circ_{298}(\text{H}_2\text{O}_2)$  (the partition function apparently does not take into account the hindered rotation in  $\text{H}_2\text{O}_2$ ). Following the same idea, but using the correct value of  $D_0(\text{H-OH})$  of Harich *et al.*<sup>5</sup> and utilizing  $D_0(\text{HO-OH})$  of Luo *et al.*<sup>37</sup> in conjunction with  $\Delta_f H^\circ_{298}(\text{H}_2\text{O}_2) = -135.88 \pm 0.22 \text{ kJ mol}^{-1}$  and  $[H^\circ(298.15 \text{ K}) - H^\circ(0 \text{ K})] \times (\text{H}_2\text{O}_2) = 11.158 \text{ kJ mol}^{-1}$  from Gurvich *et al.*,<sup>16</sup> together with other auxiliary thermochemical values given in (1a) and (1c) above, leads to  $\Delta_f H^\circ_0(\text{OH}) = 37.32 \pm 0.07$  and  $37.05 \pm 0.11 \text{ kJ mol}^{-1}$ , respectively. The two values differ by 23 cm<sup>-1</sup>, rather than by 10 cm<sup>-1</sup>, and yield an arithmetic average of  $\Delta_f H^\circ_0(\text{OH}) = 37.18 \pm 1.71 \text{ kJ mol}^{-1}$  and a weighted average of  $\Delta_f H^\circ_0(\text{OH}) = 37.24 \pm 1.56 \text{ kJ mol}^{-1}$ , where in both cases the uncertainty reflects a 95% confidence limit. The weighted average corresponds to  $\Delta_f H^\circ_{298}(\text{OH}) = 37.48 \pm 1.56 \text{ kJ mol}^{-1}$ .

(1z) A critical evaluation of competing and mutually exclusive values for OH, one arising from the best available values for  $D_0(\text{H-OH})$  [see (1c)–(1f) above], the other from the

best available value for  $D_0(\text{OH})$  [see (1a) and (1b) above]. The evaluation considers both types of measurements as well as high-level calculations [see (1m) above]. The recommended value corresponds to the experimental consensus value  $D_0(\text{H-OH}) = 41\,128 \pm 24 \text{ cm}^{-1} = 429.00 \pm 0.29 \text{ kJ mol}^{-1}$  [see (1f) above].

(1aa) Critical evaluation of atmospherically relevant kinetic data. The quoted value is from Ruscic *et al.*<sup>4</sup> [see (1d) above].

(1bb) An unevaluated tabulation of available values, listing the thermochemistry of OH from NIST-JANAF Tables.<sup>35</sup>

### Preferred Value of the Enthalpy of Formation

$$\Delta_f H^\circ(298.15 \text{ K}) = 37.3 \pm 0.3 \text{ kJ mol}^{-1}$$

$$\Delta_f H^\circ(0 \text{ K}) = 37.1 \pm 0.3 \text{ kJ mol}^{-1}$$

The preferred value is based on the consensus value obtained from photoionization measurements, as analyzed in detail by Ruscic *et al.*<sup>6</sup> There are essentially two contending values for the enthalpy of formation of OH: a higher value based on  $D_0(\text{OH})$  that was obtained by extrapolating the spectroscopic observations on OH, and a lower value based on  $D_0(\text{H-OH})$  that was obtained primarily from photoionization data used in a positive ion cycle. The difference between the two possible values for  $\Delta_f H^\circ(\text{OH})$  is 2.1 kJ mol<sup>-1</sup>. Recently, Ruscic *et al.*<sup>4,6</sup> have shown why the spectroscopic extrapolation leading to a higher enthalpy of OH is in error and have produced several careful photoionization measurements that very strongly support the lower value. Additional independent support for the lower value is lent by new photodissociation<sup>5</sup> and kinetic<sup>7</sup> experiments. The kinetic measurement produces a value identical to the consensus photoionization value, albeit with a larger error bar. The very small remaining inconsistency ( $< 0.28 \text{ kJ mol}^{-1}$ ) between the consensus photoionization value and the photodissociation value has been also discussed by Ruscic *et al.*<sup>6</sup>

The preferred value corresponds to the recommended values of the O–H bond dissociation energy of water  $D_0(\text{H-OH}) = 492.01 \pm 0.29 \text{ kJ mol}^{-1}$  ( $497.11 \pm 0.29 \text{ kJ mol}^{-1}$  at 298.15 K) and that of hydroxyl  $D_0(\text{OH}) = 425.79 \pm 0.30 \text{ kJ mol}^{-1}$  ( $429.90 \pm 0.30 \text{ kJ mol}^{-1}$  at 298.15 K) when used with  $[H^\circ(298.15 \text{ K}) - H^\circ(0 \text{ K})](\text{OH}) = 8.813 \text{ kJ mol}^{-1}$  from Gurvich *et al.*,<sup>16</sup> together with CODATA<sup>26</sup> recommended values  $\Delta_f H^\circ_{298}(\text{H}) = 217.998 \pm 0.006 \text{ kJ mol}^{-1}$ ,  $[H^\circ(298.15 \text{ K}) - H^\circ(0 \text{ K})](\text{H}) = 6.197 \pm 0.001 \text{ kJ mol}^{-1}$ ,  $[H^\circ(298.15 \text{ K}) - H^\circ(0 \text{ K})](\text{H}_2) = 8.468 \pm 0.001 \text{ kJ mol}^{-1}$ ,  $\Delta_f H^\circ_{298}(\text{O}) = 249.18 \pm 0.10 \text{ kJ mol}^{-1}$ ,  $[H^\circ(298.15 \text{ K}) - H^\circ(0 \text{ K})](\text{O}) = 6.725 \pm 0.001 \text{ kJ mol}^{-1}$ ,  $[H^\circ(298.15 \text{ K}) - H^\circ(0 \text{ K})](\text{O}_2) = 8.680 \pm 0.002 \text{ kJ mol}^{-1}$ ,  $\Delta_f H^\circ_{298}(\text{H}_2\text{O}) = -241.826 \pm 0.040 \text{ kJ mol}^{-1}$ ,  $[H^\circ(298.15 \text{ K}) - H^\circ(0 \text{ K})](\text{H}_2\text{O}) = 9.905 \pm 0.005 \text{ kJ mol}^{-1}$ .



Geometry (distance in Å) <sup>(2a)</sup>					
Z matrix		Cartesian coordinates			
		x	y	z	
O		O	0.000 000	0.000 000	-0.057 476
H	1 0.969 66	H	0.000 000	0.000 000	0.912 184

Moments of inertia in the electronic ground state<sup>(2b)</sup>  
 $I_B = 1.509 \times 10^{-47} \text{ kg m}^2$

Vibrational wave numbers in the electronic ground state  $\nu_i(\text{cm}^{-1})$ <sup>(2c)</sup>  
 3569.64 ( $\sigma$ )

---

Heat Capacity $C_p^\circ$ , Entropy $S^\circ$ , and Enthalpy Increment $[H^\circ(T) - H^\circ(0 \text{ K})]$ <sup>(2d),(2e)</sup>			
T/K	$C_p^\circ(T)$ ( $\text{J K}^{-1} \text{ mol}^{-1}$ )	$S^\circ(T)$ ( $\text{J K}^{-1} \text{ mol}^{-1}$ )	$[H^\circ(T) - H^\circ(0 \text{ K})]$ ( $\text{kJ mol}^{-1}$ )
150	31.087	162.828	4.314
200	30.515	171.688	5.853
250	30.131	178.454	7.371
298.15	29.886	183.737	8.813
300	29.879	183.922	8.869
350	29.714	188.514	10.357
400	29.604	192.474	11.840
500	29.495	199.066	14.795
600	29.513	204.443	17.744
800	29.914	212.977	23.678
1000	30.682	219.730	29.734
1200	31.603	225.405	35.962
1500	32.956	232.605	45.650
2000	34.766	242.348	62.606
2500	36.060	250.252	80.327
3000	37.036	256.917	98.613

## 7-Constant NASA Polynomial

```

HYDROXYL RADICAL JUN03 O 1.H 1. 0. 0.G 200.000 6000.000 17.00734 1
0.28385303E+01 0.11074129E-02-0.29400021E-06 0.42069873E-10-0.24228989E-14 2
0.36978081E+04 0.58449465E+01 0.39919842E+01-0.24010666E-02 0.46166403E-05 3
-0.38791631E-08 0.13631950E-11 0.33688984E+04-0.10399848E+00 0.44861538E+04 4

```

## 9-Constant NASA Polynomial

```

HYDROXYL RADICAL IUPAC Task Group on Selected Radicals
2 JUN03 O 1.00H 1.00 0.00 0.00 0.00 0 17.00734 37300.000
200.000 1000.0007 -2.0 -1.0 0.0 1.0 2.0 3.0 4.0 0.0 8813.000
-0.251176012D+04 0.100200647D+03 0.301176222D+01 0.163498343D-02-0.330846245D-05
0.342402920D-08-0.116985048D-11 0.000000000D+00 0.295921560D+04 0.489223824D+01
1000.000 6000.0007 -2.0 -1.0 0.0 1.0 2.0 3.0 4.0 0.0 8813.000
0.101506100D+07-0.250398392D+04 0.511068667D+01 0.133362531D-03-0.835729831D-07
0.201593585D-10-0.156182738D-14 0.000000000D+00 0.201600906D+05-0.109702891D+02

```

### Comments on Molecular Data, Heat Capacity, Entropy, and Enthalpy Increment

(2a) The geometry reflects<sup>28</sup>  $r_e(\text{OH}) = 0.9696_6 \text{ \AA}$ , congruent with  $B_e = 18.910_8 \text{ cm}^{-1}$ .

(2b) The listed moment of inertia is based on the experimental rotational constant<sup>28</sup>  $B_0 = 18.550_4 \text{ cm}^{-1}$ .

(2c) The listed vibrational frequency is the fundamental,

$\Delta G_{1/2}$ , corresponding<sup>28</sup> to  $\omega_e = 3737.76_1 \text{ cm}^{-1}$ ,  $\omega_e x_e = -84.88_1 \text{ cm}^{-1}$ ,  $\omega_e y_e = 0.54_1 \text{ cm}^{-1}$ .

(2d) The heat capacity, entropy, and enthalpy increment values are adopted from Gurvich *et al.*<sup>16</sup> These authors calculated the thermodynamic functions for OH by direct summation over the rovibrational levels of  $\tilde{X}^2\Pi$ ,  $\tilde{A}^2\Sigma$ , and  $\tilde{B}^2\Sigma$  states, terminating appropriately the summations in accord

with estimated limiting curves of dissociation for these states.

(2e) The standard heat capacity, entropy, and enthalpy increment values reported in the NBS Tables<sup>13</sup> are  $C_p^\circ(298.15\text{ K}) = 29.886\text{ J mol}^{-1}\text{ K}^{-1}$ ,  $S^\circ(298.15\text{ K}) = 183.745\text{ J mol}^{-1}\text{ K}^{-1}$ ,  $[H^\circ(298.15\text{ K}) - H^\circ(0\text{ K})](\text{OH}) = 8.816\text{ kJ mol}^{-1}$ . The values listed in the JANAF<sup>15</sup> and NIST-JANAF<sup>35</sup> thermochemical tables are wrong, particularly at higher temperatures, since that compilation does not take into account properly the degeneracy and multiplicity of the ground electronic state of OH [the listed values are  $C_p^\circ(298.15\text{ K}) = 29.986\text{ J mol}^{-1}\text{ K}^{-1}$ ,  $S^\circ(298.15\text{ K}) = 183.708\text{ J mol}^{-1}\text{ K}^{-1}$ ,  $H^\circ(298.15\text{ K}) - H^\circ(0\text{ K}) = 9.172\text{ kJ mol}^{-1}$ ]. In addition, their temperature corrections for the enthalpy of formation are both erroneous and incongruent with the listed enthalpy increments [see also (1q) above]. The *Thermochemical Database for Combustion*<sup>22</sup> lists values in full accord with the compilation by Gurvich *et al.*<sup>16</sup>  $C_p^\circ(298.15\text{ K}) = 29.886\text{ J mol}^{-1}\text{ K}^{-1}$  and  $S^\circ(298.15\text{ K}) = 183.74\text{ J mol}^{-1}\text{ K}^{-1}$ . The values obtained from G3MP2B3 computations<sup>12</sup> are  $C_p^\circ(298.15\text{ K}) = 29.15\text{ J mol}^{-1}\text{ K}^{-1}$ ,  $S^\circ(298.15\text{ K}) = 184.05\text{ J mol}^{-1}\text{ K}^{-1}$ ,  $H^\circ(298.15\text{ K}) - H^\circ(0\text{ K}) = 8.68\text{ kJ mol}^{-1}$ .

## References

- R. F. Barrow, *Ark. Fys.* **11**, 281 (1956).
- C. Carlone and F. W. Dalby, *Can. J. Phys.* **47**, 1945 (1969).
- K. E. McCulloh, *Int. J. Mass Spectrom.* **21**, 333 (1976).
- B. Ruscic, D. Feller, D. A. Dixon, K. A. Peterson, L. B. Harding, R. L. Asher, and A. F. Wagner, *J. Phys. Chem. A* **105**, 1 (2001).
- S. A. Harich, D. W. H. Hwang, X. Yang, J. J. Lin, X. Yang, and R. N. Dixon, *J. Chem. Phys.* **113**, 10073 (2000).
- B. Ruscic, A. F. Wagner, L. B. Harding, R. L. Asher, D. Feller, D. A. Dixon, K. A. Peterson, Y. Song, X. Qian, C.-Y. Ng, J. Liu, W. Chen, and D. W. Schwenke, *J. Phys. Chem. A* **106**, 2727 (2002).
- J. T. Herbon, R. K. Hanson, D. M. Golden, and C. T. Bowman, 29th International Symposium on Combustion, Hokkaido, Japan, July 21–26, 2002.
- C. F. Melius, *Thermochemical Modeling: I. Application to Decomposition of Energetic Materials*, in *Chemistry and Physics of Energetic Materials*, edited by S. N. Bulusu (Kluwer, Dordrecht, 1990); see also (<http://z.ca.sandia.gov/~melius/>)
- L. A. Curtiss, K. Raghavachari, P. C. Redfern, and B. B. Stefanov, *J. Chem. Phys.* **108**, 692 (1998).
- L. A. Curtiss, K. Raghavachari, P. C. Redfern, V. Rassolov, and J. A. Pople, *J. Chem. Phys.* **109**, 7764 (1998).
- S. Parthiban and J. M. L. Martin, *J. Chem. Phys.* **114**, 6014 (2001).
- R. Janoschek and M. J. Rossi, *Int. J. Chem. Kinet.* **34**, 550 (2002).
- D. D. Wagman, W. E. Evans, V. B. Parker, R. H. Schumm, I. Halow, S. M. Bailey, K. L. Churney, and R. L. Nuttall, *The NBS Tables of Chemical Thermodynamic Properties*, *J. Phys. Chem. Ref. Data* **11**, Suppl. 2 (1982).
- D. F. McMillen and D. M. Golden, *Ann. Rev. Phys. Chem.* **33**, 493 (1982).
- M. W. Chase, Jr., C. A. Davies, J. R. Downey, Jr., D. J. Frurip, R. A. McDonald, and A. N. Syverud, *JANAF Thermochemical Tables*, 3rd ed., *J. Phys. Chem. Ref. Data* **14**, Suppl. 1 (1985).
- L. V. Gurvich, I. V. Veits, and C. B. Alcock, *Thermodynamic Properties of Individual Substances*, 4th ed. (Hemisphere, New York, 1989), Vol. 1.
- J. Berkowitz, G. B. Ellison, and D. Gutman, *J. Phys. Chem.* **98**, 2744 (1994).
- Computational Chemistry Comparison and Benchmark DataBase (CCCBDB), NIST 1999; see (<http://srdata.nist.gov/cccbdb/>)
- Standard Thermodynamic Properties of Chemical Substances*, in *CRC Handbook of Chemistry and Physics*, edited by D. Lide, 82nd ed. (CRC, Boca Raton, FL, 2001–2002).
- J. A. Kerr and D. W. Stocker, *Strengths of Chemical Bonds*, in *CRC Handbook of Chemistry and Physics*, edited by D. Lide, 82nd ed. (CRC, Boca Raton, FL, 2001–2002).
- R. Atkinson, D. L. Baulch, R. A. Cox, R. F. Hampson, Jr., J. A. Kerr, M. J. Rossi, and J. Troe, *J. Phys. Chem. Ref. Data* **29**, 167 (2000).
- A. Burcat, TAE Report No. 867, Technion, Haifa, 2001; see also (<ftp://ftp.technion.ac.il/pub/supported/aetdd/thermodynamics>)
- J. A. Joens, *J. Phys. Chem. A* **105**, 11041 (2001).
- S. P. Sander, R. R. Friedl, D. M. Golden, M. J. Kurylo, R. E. Huie, V. L. Orkin, G. K. Moortgat, A. R. Ravishankara, C. E. Kolb, M. J. Molina, and B. J. Finlayson-Pitts, JPL Publication 02-25, NASA and JPL, February 1, 2003.
- H. Y. Afeefy, J. F. Liebman, and S. E. Stein, *Neutral Thermochemical Data*, in *NIST Chemistry WebBook*, NIST Standard Reference Database Number 69, edited by P. J. Linstrom and W. G. Mallard (NIST, Gaithersburg, MD, 2003); (<http://webbook.nist.gov/>)
- J. D. Cox, D. D. Wagman, and V. A. Medvedev, *CODATA Key Values for Thermodynamics* (Hemisphere, New York, 1989); see also (<http://www.codata.org/codata/databases/key1.html>)
- G. H. Dieke and H. M. Crosswhite, *The Ultraviolet Bands of OH Fundamental Data*, Bumblebee Series Report No. 87 (Johns Hopkins University Press, Baltimore, MD, 1948); see also G. H. Dieke and H. M. Crosswhite, *J. Quant. Spectrosc. Radiant. Transfer* **2**, 97 (1962).
- K. Huber and G. Herzberg, *Molecular Spectra and Molecular Structure. IV. Constants of Diatomic Molecules* (Van Nostrand, New York, 1979).
- C. E. Moore, *Atomic Energy Levels*; NBS Circ 467 (U.S. National Bureau of Standards, Washington, D.C., 1949), Vol. 1.
- D. R. Stull and H. Prophet, *JANAF Thermochemical Tables*, 2nd ed. NSRDS-NBS 37 (US Gov. Printing Office, Washington, DC, 1971).
- R. T. Wiedmann, R. G. Tonkyn, and M. G. White, *J. Chem. Phys.* **97**, 768 (1992).
- L. A. Curtiss, P. C. Redfern, K. Raghavachari, V. Rassolov, and J. A. Pople, *J. Chem. Phys.* **110**, 4703 (1999).
- L. A. Curtiss, K. Raghavachari, G. W. Trucks, and J. A. Pople, *J. Chem. Phys.* **94**, 7221 (1991).
- A. G. Baboul, L. A. Curtiss, P. C. Redfern, and K. Raghavachari, *J. Chem. Phys.* **110**, 7650 (1999).
- M. W. Chase, Jr., *NIST-JANAF Thermochemical Tables*, 4th ed., *J. Phys. Chem. Ref. Data Monogr.* 9 (1998).
- V. P. Glushko, L. V. Gurvich, G. A. Bergman, I. V. Veits, V. A. Medvedev, G. A. Khackhuruzov, and V. S. Yungman, *Termodinamicheski Svoistva Individual'nikh Veschestv*, 3rd ed. (Nauka, Moscow, 1979).
- X. Luo, P. R. Fleming, and T. R. Rizzo, *J. Chem. Phys.* **96**, 5659 (1992).

7.3.2. CH<sub>3</sub>O Radical

## 7.3.2. Methoxyl radical

2143-68-2

CH <sub>3</sub> O( <sup>2</sup> E)	C <sub>3v</sub> (σ <sub>ext</sub> =3)
Δ <sub>f</sub> H°(298.15 K) = 21.0 ± 2.1 kJ mol <sup>-1</sup>	Δ <sub>f</sub> H°(0 K) = 28.4 ± 2.1 kJ mol <sup>-1</sup>
C° <sub>p</sub> (298.15 K) = 42.541 J K <sup>-1</sup> mol <sup>-1</sup>	H°(298.15 K) - H°(0 K) = 10.719 kJ mol <sup>-1</sup>
S°(298.15 K) = 234.278 J K <sup>-1</sup> mol <sup>-1</sup>	p° = 100 000 Pa (1 bar)

## Literature Data for the Enthalpy of Formation at 298.15 K

Δ <sub>f</sub> H°(kJ mol <sup>-1</sup> )	Authors and Reference	Method <sup>a</sup>	Comments
<b>Measurements</b>			
23.4 ± 6 <sup>c</sup>	Holmes and Lossing (1984) <sup>1</sup>	EIMS-PIC	(1a)
15.3 <sup>b</sup> ± 5.7 <sup>c</sup>	Meot-Ner and Sieck (1986) <sup>2</sup>	MSE-NIC	(1b)
22.1 <sup>b</sup> ± 1.4 <sup>c</sup>	Osborn <i>et al.</i> (1995) <sup>3</sup>	DD	(1c)
20.7 <sup>b</sup> ± 1.9 <sup>c</sup>	Dertinger <i>et al.</i> (1995) <sup>4</sup>	DD	(1d)
19.1 <sup>b</sup> ± 2.4 <sup>c</sup>	DeTuri and Ervin (1999) <sup>5</sup>	TCID-NIC	(1e)
<b>Computations</b>			
25.8 <sup>b</sup> ± 8.4	Bauschlicher, Jr. <i>et al.</i> (1992) <sup>6</sup>	MCPF	(1f)
27.6 ± 9.2 <sup>c</sup>	Zachariah <i>et al.</i> (1996) <sup>7</sup>	BAC-MP4	(1g)
21.8 ± 13 <sup>c</sup>	Curtiss <i>et al.</i> (1998) <sup>8</sup>	CBS-Q	(1h)
20.5 ± 7.9 <sup>c</sup>	Curtiss <i>et al.</i> (1998) <sup>9</sup>	G3	(1i)
18.6 ± 1.9 <sup>c</sup>	Parthiban and Martin (2002) <sup>10</sup>	W2	(1j)
19.2 ± 7.8 <sup>c</sup>	Janoschek and Rossi (2002) <sup>11</sup>	G3MP2B3	(1k)
19.7 <sup>b</sup>	Petraco <i>et al.</i> (2002) <sup>12</sup>	RCCSD(T)	(1l)
<b>Reviews and Evaluations</b>			
17.6 ± 4.2	McMillen and Golden (1982) <sup>13</sup>	CDE	(1m)
16.2	Batt (1987) <sup>14</sup>	CDE	(1n)
16.7 ± 4.2	Ruscic and Berkowitz (1991) <sup>15</sup>	CDE	(1o)
13 ± 4	Gurvich <i>et al.</i> (1991) <sup>16</sup>	CDE	(1p)
12.2	Kuo <i>et al.</i> (1994) <sup>17</sup>	CDE	(1q)
17.2 ± 3.8	Berkowitz <i>et al.</i> (1994) <sup>18</sup>	CDE	(1r)
13.0 ± 4.0	NIST CCCBDB (1999) <sup>19</sup>	TT-A	(1s)
17.2 ± 3.8	Atkinson <i>et al.</i> (2000) <sup>20</sup>	TT-A	(1t)
17.2 ± 3.8	Kerr and Stocker (2000) <sup>21</sup>	TT-A	(1u)
16.3	Burcat (2001) <sup>22</sup>	TT-A	(1v)
17.15 ± 3.8	Sander <i>et al.</i> (2003) <sup>23</sup>	TT-A	(1w)
17 ± 4	NIST WebBook (2003) <sup>24</sup>	TT-A	(1x)

<sup>a</sup>EIMS-PIC: positive ion cycle based on combining electron impact mass-spectrometric measurements of appearance energy from a stable molecule with ionization energy of the radical; MSE-NIC: negative ion cycle based on combining mass-spectrometric equilibrium measurements with electron affinity of the radical; DD: radical dissociation dynamics study; TCID-NIC: negative ion cycle based on combining energy-resolved threshold collision-induced dissociation measurements of proton-bound complex with electron affinity of the hydrocarbon radical from negative ion photoelectron spectroscopy; CDE: critical data evaluation; and TT-A: annotated tabulation of thermodynamic data.

<sup>b</sup>The quoted value was either not given explicitly by the author(s) or it was recalculated using auxiliary thermochemical values that differ from those used by the original authors; see individual comments for additional details.

<sup>c</sup>The uncertainty was either not given explicitly by the original author(s) or it has been modified; see individual comments for further explanations.

**Comments on the Enthalpies of Formation**

(1a) A determination of the electron-impact appearance energies  $E_{\text{ap}}(\text{CH}_3\text{OCH}_2^+ / (\text{CH}_3\text{O})_2\text{CH}_2) = 10.69 \pm 0.05$  eV and  $E_{\text{ap}}(\text{CH}_3\text{OC}^+\text{HCH}_3 / (\text{CH}_3\text{O})_2\text{CHCH}_3) = 9.98 \pm 0.05$  eV.

The enthalpy of formation for CH<sub>3</sub>O was derived using the electron-impact literature values<sup>25</sup> of Δ<sub>f</sub>H°<sub>298</sub>(CH<sub>3</sub>OCH<sub>2</sub><sup>+</sup>) = 656.9 kJ mol<sup>-1</sup> and Δ<sub>f</sub>H°<sub>298</sub>(CH<sub>3</sub>OC<sup>+</sup>HCH<sub>3</sub>) = 552.3 kJ mol<sup>-1</sup>. The reported Δ<sub>f</sub>H°<sub>298</sub>(CH<sub>3</sub>O) = 23.4 kJ mol<sup>-1</sup> (5.6 kcal mol<sup>-1</sup>) is the average of the derived 6.2 and 5.0 kcal mol<sup>-1</sup> values. The authors do not give an explicit uncertainty estimate. The assigned uncertainty re-

fects the disparity between the two measurements.

(1b) A measurement of gas-phase acidity of CH<sub>3</sub>OH relative to the gas-phase acidity of H<sub>2</sub>O by variable-temperature pulsed high-pressure mass spectrometry. The difference in the enthalpy of deprotonation, Δ<sub>acid</sub>H°<sub>300</sub>(H<sub>2</sub>O) - Δ<sub>acid</sub>H°<sub>300</sub>(CH<sub>3</sub>OH), was found to be 38.5 ± 0.8 kJ mol<sup>-1</sup> (9.2 ± 0.2 kcal mol<sup>-1</sup>). Using an older value for the enthalpy of deprotonation of water, the authors obtain Δ<sub>acid</sub>H°<sub>0</sub>(CH<sub>3</sub>OH) = 1597 ± 3 kJ mol<sup>-1</sup>. Keeping all else the same, but introducing the new value Δ<sub>acid</sub>H°<sub>298</sub>(H<sub>2</sub>O) = 1632.6 ± 0.3 kJ mol<sup>-1</sup> from Ruscic *et al.*,<sup>26</sup> results in

$\Delta_{\text{acid}}H^{\circ}_{298}(\text{CH}_3\text{OH}) = 1594.1 \pm 0.8 \text{ kJ mol}^{-1}$ . This further changes to  $\Delta_{\text{acid}}H^{\circ}_0(\text{CH}_3\text{OH}) = 1589.2 \pm 0.8 \text{ kJ mol}^{-1}$  if one uses  $[H^{\circ}(298.15 \text{ K}) - H^{\circ}(0 \text{ K})](\text{CH}_3\text{OH}) = 11.441 \text{ kJ mol}^{-1}$  and  $[H^{\circ}(298.15 \text{ K}) - H^{\circ}(0 \text{ K})](\text{H}^+) = 6.197 \text{ kJ mol}^{-1}$  from Gurvich *et al.*<sup>16,27</sup> and  $[H^{\circ}(298.15 \text{ K}) - H^{\circ}(0 \text{ K})](\text{CH}_3\text{O}^-) = 10.101 \text{ kJ mol}^{-1}$  from Ruscic<sup>28</sup> (estimated from scaled frequencies of  $\text{CH}_3\text{O}^-$  calculated at the B3LYP/6-31G(d) level of theory). With the electron affinity  $E_{\text{ea}}(\text{CH}_3\text{O}) = 1.572 \pm 0.004 \text{ eV}$  from Ramond *et al.*<sup>29</sup> and the ionization energy  $E_i(\text{H})/hc = 109\,678.773\,704 \pm 0.000\,006 \text{ cm}^{-1}$  from Erickson<sup>30</sup> one obtains the bond dissociation energy  $D_0(\text{CH}_3\text{O}-\text{H}) = 428.9 \pm 0.9 \text{ kJ mol}^{-1}$  ( $434.3 \pm 0.9 \text{ kJ mol}^{-1}$  at  $298.15 \text{ K}$ ). Using  $\Delta_f H^{\circ}_{298}(\text{CH}_3\text{OH}) = -201.0 \pm 0.6 \text{ kJ mol}^{-1}$  from Gurvich *et al.*<sup>16</sup> results in  $\Delta_f H^{\circ}_{298}(\text{CH}_3\text{O}) = 15.3 \pm 1.1 \text{ kJ mol}^{-1}$ . The slightly different electron affinity value of Osborn *et al.*<sup>31</sup>  $E_{\text{ea}}(\text{CH}_3\text{O}) = 1.568 \pm 0.005 \text{ eV}$  would result in  $\Delta_f H^{\circ}_{298}(\text{CH}_3\text{O}) = 15.0 \pm 1.2 \text{ kJ mol}^{-1}$ . As a consequence of the linear analysis discussed in conjunction with the selection of the preferred value (see below), the uncertainty given in the table,  $\pm 5.7 \text{ kJ mol}^{-1}$ , is substantially larger than the  $\pm 1.1 \text{ kJ mol}^{-1}$  that would result from the original data given by Meot-Ner and Sieck.<sup>2</sup>

(1c) The dissociation dynamics of  $\text{CH}_3\text{O}$  following  $\tilde{A}^2 A_1 \leftarrow \tilde{X}^2 E$  transition examined using photofragment translational spectroscopy. The authors find by conservation of energy that the bond dissociation energy of  $D_0(\text{CH}_3-\text{O}) = 367.4 \pm 1.3 \text{ kJ mol}^{-1}$  ( $87.8 \pm 0.3 \text{ kcal mol}^{-1}$ ) is consistent with all measured photofragment translational energy spectra, assuming that at least some ground state methyl radicals are produced during the experiment. Using the enthalpy of formation of  $\text{CH}_3$  from JANAF,<sup>32,33</sup> the authors obtain  $\Delta_f H^{\circ}_0(\text{CH}_3\text{O}) = 28.5 \pm 1.7 \text{ kJ mol}^{-1}$  and, with the estimated integrated heat capacities of Ruscic and Berkowitz,<sup>15</sup>  $\Delta_f H^{\circ}_{298}(\text{CH}_3\text{O}) = 20.5 \pm 1.7 \text{ kJ mol}^{-1}$ . However, the preferred value from the current compilation,  $\Delta_f H^{\circ}_0(\text{CH}_3) = 150.0 \pm 0.3 \text{ kJ mol}^{-1}$ , in conjunction with the standard value<sup>27,32</sup>  $\Delta_f H^{\circ}_0(\text{O}) = 246.795 \pm 0.10 \text{ kJ mol}^{-1}$ , leads to  $\Delta_f H^{\circ}_0(\text{CH}_3\text{O}) = 29.4 \pm 1.3 \text{ kJ mol}^{-1}$  and  $\Delta_f H^{\circ}_{298}(\text{CH}_3\text{O}) = 22.1 \pm 1.4 \text{ kJ mol}^{-1}$ .

(1d) Vibration-rotation state-resolved study of the unimolecular dissociation dynamics of highly vibrationally excited  $\text{CH}_3\text{O}$  performed over a wide range of excitation energies using stimulated emission pumping-laser induced fluorescence technique. Rovibrational quantum-state resolved unimolecular dissociation rates of highly excited methoxyl radicals over a  $3000 \text{ cm}^{-1}$  range of energies were used to obtain statistical rate constants  $k(E, J)$ , which were then fit to a conventional RRKM expression, modified to include hydrogen atom tunneling through an association barrier of  $1560 \pm 150 \text{ cm}^{-1}$ . A value of  $D_0(\text{H}-\text{CH}_2\text{O}) = 6950 \pm 150 \text{ cm}^{-1}$  gives the best fit of the calculated decomposition rate coefficients to the experimental data. Using  $\Delta_f H^{\circ}_0(\text{CH}_2\text{O}) = -104.862 \pm 0.5 \text{ kJ mol}^{-1}$  from Gurvich *et al.*<sup>16</sup> and the standard value<sup>16,32</sup>  $\Delta_f H^{\circ}_0(\text{H}) = 216.035 \pm 0.006 \text{ kJ mol}^{-1}$ , one obtains  $\Delta_f H^{\circ}_0(\text{CH}_3\text{O}) = 28.0 \pm 1.9 \text{ kJ mol}^{-1}$  and

$$\Delta_f H^{\circ}_{298}(\text{CH}_3\text{O}) = 20.7 \pm 1.9 \text{ kJ mol}^{-1}.$$

(1e) Gas-phase acidity of methanol from energy-resolved threshold collision-induced dissociation (TCID) measurements of the fluoride-methanol, methoxide-water, and methoxide-methanol proton-bound complexes. The competitive dissociation reactions of the alkoxide-water complexes were studied using a guided ion beam tandem mass spectrometer, where the reaction cross sections and product branching fractions to the two proton transfer channels were measured as a function of collision energy. From the RRKM-modeled enthalpy difference between the product channels, the gas-phase acidity of  $\Delta_{\text{acid}}H^{\circ}_0(\text{CH}_3\text{OH}) = 1594 \pm 3 \text{ kJ mol}^{-1}$  was determined. In light of a change in the gas-phase acidity of water by Ruscic *et al.*,<sup>26</sup> this value was subsequently revised downward by Ervin and DeTuri<sup>34</sup> to  $1593.0 \pm 2.3 \text{ kJ mol}^{-1}$ . Using the electron affinity  $E_{\text{ea}}(\text{CH}_3\text{O}) = 1.572 \pm 0.004 \text{ eV}$  from Ramond *et al.*<sup>29</sup> and other auxiliary thermochemical quantities as in (1b) above results in the O-H bond dissociation energy  $D_0(\text{CH}_3\text{O}-\text{H}) = 432.6 \pm 2.3 \text{ kJ mol}^{-1}$  ( $438.1 \pm 2.3 \text{ kJ mol}^{-1}$  at  $298.15 \text{ K}$ ) and  $\Delta_f H^{\circ}_{298}(\text{CH}_3\text{O}) = 19.1 \pm 2.4 \text{ kJ mol}^{-1}$ . The slightly different electron affinity value of Osborn *et al.*,<sup>31</sup>  $E_{\text{ea}}(\text{CH}_3\text{O}) = 1.568 \pm 0.005 \text{ eV}$ , would produce  $\Delta_f H^{\circ}_{298}(\text{CH}_3\text{O}) = 18.7 \pm 2.4 \text{ kJ mol}^{-1}$ .

(1f) The MCPF method. Using a large basis set, the O-H bond dissociation energy in  $\text{CH}_3\text{OH}$  was calculated to be  $D_0(\text{CH}_3\text{O}-\text{H}) = 101.0 \text{ kcal mol}^{-1} = 422.6 \text{ kJ mol}^{-1}$ . Based on previous experiences, the authors have added  $4 \text{ kcal mol}^{-1}$  to the computed O-H bond dissociation energy resulting in  $105.0 \pm 2 \text{ kcal mol}^{-1} = 439.3 \pm 8.4 \text{ kJ mol}^{-1}$ . Taking into account the enthalpy increments as listed in (1b) above, one obtains the O-H bond dissociation energy of methanol of  $444.8 \pm 8.4 \text{ kJ mol}^{-1}$  at  $298.15 \text{ K}$ . With the enthalpy of formation of methanol of Gurvich *et al.*<sup>16</sup> [see (1b) above], the reported O-H bond dissociation energy corresponds to  $\Delta_f H^{\circ}_0(\text{CH}_3\text{O}) = 25.8 \pm 8.4 \text{ kJ mol}^{-1}$ .

(1g) BAC-MP4 *ab initio* computations. Note that the same result was subsequently obtained by Caralp *et al.*<sup>35</sup> The originally quoted uncertainty of  $\pm 4.6 \text{ kJ mol}^{-1}$  was multiplied by factor of 2 to bring it closer to the desired 95% confidence limit.

(1h) CBS-Q calculation. The reported average absolute deviation of  $1.57 \text{ kcal mol}^{-1}$  was multiplied by 2 to bring it closer to the desired 95% confidence limit. The equivalent CBS-q and CBS-4 enthalpies of formation are  $31.8 \pm 18 \text{ kJ mol}^{-1}$  ( $7.6 \text{ kcal mol}^{-1}$ ) and  $31.0 \pm 26 \text{ kJ mol}^{-1}$  ( $7.4 \text{ kcal mol}^{-1}$ ), where the uncertainties have been obtained in an analogous way.

(1i) G3 *ab initio* calculation. The value listed in the table is converted from  $4.9 \text{ kcal mol}^{-1}$ . The uncertainty quoted in the table corresponds approximately to 95% confidence limits, based on twice the average absolute deviation of  $0.94 \text{ kcal mol}^{-1}$  for the enthalpies in the G2/97 test set, which roughly corresponds to 1 s.d. At the G3(MP2) level of theory<sup>36</sup>  $\Delta_f H^{\circ}_{298}(\text{CH}_3\text{O}) = 22.2 \pm 9.9 \text{ kJ mol}^{-1}$  ( $5.3 \text{ kcal mol}^{-1}$ ), where the quoted uncertainty was derived in a similar fashion as for the G3 value. At the G2 level of

theory<sup>37</sup>  $\Delta_f H^\circ_{298}(\text{CH}_3\text{O}) = 20.1 \pm 13.1 \text{ kJ mol}^{-1}$  (4.8 kcal mol<sup>-1</sup>).

(1j) W2 *ab initio* calculation. The uncertainty quoted in the table corresponds approximately to 95% confidence limits based on twice the average absolute deviation for the W2 test set<sup>38</sup> of 0.23 kcal mol<sup>-1</sup>, which corresponds roughly to one standard deviation. At the W1 level of theory<sup>10</sup>  $\Delta_f H^\circ_{298}(\text{CH}_3\text{O}) = 17.7 \pm 3.1 \text{ kJ mol}^{-1}$ , where the uncertainty has been obtained in an analogous way.

(1k) G3(MP2)//B3LYP *ab initio* calculations for 32 selected free radicals. The uncertainty given in the table corresponds approximately to 95% confidence limits based on twice the quoted average absolute deviation of 3.9 kJ mol<sup>-1</sup> for the calculated set of radicals, which corresponds roughly to 1 s.d. Note that the average absolute deviation for all enthalpies in the G2/97 test set using the same method is very slightly larger.<sup>39</sup> 4.7 kJ mol<sup>-1</sup> [see also (1i) above].

(1l) Investigation of hydrogen atom elimination from the methoxyl radical via high-level coupled-cluster methods. The TZ2P(*f,d*) basis set was used for geometry optimization and harmonic vibrational analyses and the correlation-consistent cc-pVnZ (*n* = 2–6) series for final energetic determinations and extrapolations. Valence focal-point analyses of the vibration-less dissociation energy yield  $D_0(\text{H}-\text{CH}_2\text{O}) = 84.1 \text{ kJ mol}^{-1}$ . Using  $\Delta_f H^\circ_0(\text{CH}_2\text{O}) = -104.862 \pm 0.5 \text{ kJ mol}^{-1}$  from Gurvich *et al.*<sup>16</sup> and the standard value<sup>16,32</sup>  $\Delta_f H^\circ_0(\text{H}) = 216.035 \pm 0.006 \text{ kJ mol}^{-1}$  [as in (1d) above], one obtains  $\Delta_f H^\circ_0(\text{CH}_3\text{O}) = 27.1 \text{ kJ mol}^{-1}$  which is consistent with  $\Delta_f H^\circ_{298}(\text{CH}_3\text{O}) = 19.7 \text{ kJ mol}^{-1}$ . The authors note that the association barrier used by Dertinger *et al.*<sup>4</sup> is in good agreement with their calculated value of 1653 cm<sup>-1</sup>, and that the computed thermochemistry is in agreement with the latter work, as well as with the experimental value of Osborn *et al.*<sup>3</sup> [see (1d) and (1c) above] and with the reviewed values of Ruscic and Berkowitz<sup>15</sup> and Berkowitz *et al.*<sup>18</sup> [see (1o) and (1r) below]. (1m) Recommended value from extensive evaluation of data (mainly kinetic determinations) published until 1981. The reported value is primarily based on the kinetic determination of Batt *et al.*<sup>40</sup>

(1n) A review of kinetics and thermochemistry of alkoxy and alkyl peroxy radical reactions. The suggested thermochemical properties,  $\Delta_f H^\circ_{298}(\text{CH}_3\text{O}) = 16.2 \text{ kJ mol}^{-1}$  and  $D_{298}(\text{CH}_3\text{O}-\text{H}) = 435.2 \text{ kJ mol}^{-1}$  [obtained with auxiliary data<sup>16,41</sup> of  $\Delta_f H^\circ_{298}(\text{CH}_3\text{OH}) = -201.0 \pm 0.6 \text{ kJ mol}^{-1}$  and  $\Delta_f H^\circ_{298}(\text{H}) = 217.998 \text{ kJ mol}^{-1}$ ], are based on previous kinetic studies of dimethyl peroxy and methyl nitrate decomposition reactions.

(1o) The reported enthalpies of formation of  $\Delta_f H^\circ_{298}(\text{CH}_3\text{O}) = 16.7 \pm 4.2 \text{ kJ mol}^{-1}$  and  $\Delta_f H^\circ_0(\text{CH}_3\text{O}) = 24.7 \pm 4.2 \text{ kJ mol}^{-1}$  represent the consensus of experimental data from Batt and co-workers.<sup>40,42,43</sup>

(1p) An extensive compilation and evaluation of thermodynamic properties. The selected value of  $\Delta_f H^\circ_{298}(\text{CH}_3\text{O}) = 13 \pm 4 \text{ kJ mol}^{-1}$  is a weighted average of the results of six determinations (four kinetic<sup>44–51</sup> and two appearance potential<sup>52–54</sup>) ranging from –1 to 29 kJ mol<sup>-1</sup>, with uncer-

tainties varying between  $\pm 4$  and  $\pm 40 \text{ kJ mol}^{-1}$ . Values obtained from the kinetic investigation of the pyrolysis of dimethylperoxide were considered to be the most accurate. The value is unchanged from the previous (Russian) edition.<sup>55</sup>

(1q) An enthalpy of formation difference of  $\Delta_f H^\circ_0(\text{CH}_2\text{OH}) - \Delta_f H^\circ_0(\text{CH}_3\text{O}) = 33.5 \pm 4.0 \text{ kJ mol}^{-1}$  was selected from values reported in the literature.<sup>37,6,56</sup> This, together with the authors' derived enthalpy of formation of  $\Delta_f H^\circ_0(\text{CH}_2\text{OH}) = -13.6 \text{ kJ mol}^{-1}$  was used to obtain  $\Delta_f H^\circ_0(\text{CH}_3\text{O}) = 19.9 \text{ kJ mol}^{-1}$ , and with integrated heat capacities<sup>32,57</sup> leads to  $\Delta_f H^\circ_{298}(\text{CH}_3\text{O}) = 12.2 \text{ kJ mol}^{-1}$ . With the auxiliary thermochemical values used here [see (1b) above] their  $\Delta_f H^\circ(0 \text{ K})$  would lead to  $\Delta_f H^\circ_{298}(\text{CH}_3\text{O}) = 12.5 \text{ kJ mol}^{-1}$ .

(1r) Critical data evaluation of R–H bond dissociation energies based on three methods: kinetic determinations, positive ion cycle determinations from photoelectron/photoionization measurements, and negative ion cycle determinations from photoelectron measurements of negative ions combined with gas phase acidities. The recommended value is based on a negative ion cycle that includes the gas-phase acidity of methanol<sup>2</sup> [see (1b) above] and the electron affinity of Engelking *et al.*<sup>58</sup>

(1s) The compilation lists theoretical results at various levels of theory, but also makes a reference to one experimental benchmark. The quoted experimental benchmark value is from Gurvich *et al.*<sup>16</sup> [see (1p) above].

(1t) Critical evaluation of atmospherically relevant kinetic rates. Their table of enthalpy data lists Kerr and Stocker<sup>21</sup> [see (1u) below] as their source of  $\Delta_f H^\circ_{298}(\text{CH}_3\text{O})$ , who in turn adopt the recommendation of Berkowitz *et al.*<sup>18</sup> [see (1r) above].

(1u) Thermodynamic data compilation. The tabulation selects  $D_{298}(\text{CH}_3\text{O}-\text{H}) = 436.0 \pm 3.8 \text{ kJ mol}^{-1}$  citing Berkowitz *et al.*<sup>18</sup> as a source.

(1v) Thermodynamic database for combustion. Burcat quotes Burcat and Kudchadker<sup>59</sup> as the source of  $\Delta_f H^\circ_{298}(\text{CH}_3\text{O})$ .

(1w) Critical evaluation of atmospherically relevant kinetic data. The quoted value is from Berkowitz *et al.*<sup>18</sup>

(1x) An unevaluated tabulation of available values from other sources. The source for the listed value is quoted as Tsang,<sup>60</sup> which is a review containing critical data evaluation for selected free radicals based on kinetic measurements. However, Tsang<sup>60</sup> did not evaluate the thermochemistry of CH<sub>3</sub>O. Rather, he merely lists the (rounded-off) value given by DeMore *et al.*<sup>61</sup> [an earlier version of the JPL compilation,<sup>23</sup> see (1w) above], who apparently adopt the value suggested by Ruscic and Berkowitz<sup>15</sup> [see (1o) above].

### Preferred Value of the Enthalpy of Formation

$$\Delta_f H^\circ(298.15 \text{ K}) = 21.0 \pm 2.1 \text{ kJ mol}^{-1}$$

$$\Delta_f H^\circ(0 \text{ K}) = 28.4 \pm 2.1 \text{ kJ mol}^{-1}$$

In the present context, the usefulness of the electron-impact mass-spectrometric determination of Holmes and Lossing<sup>1</sup> is somewhat limited by the relatively large associ-

ated uncertainty. Also, there is a clear discrepancy between the older (Meot-Ner and Sieck<sup>2</sup>) and the more recent (DeTuri and Ervin<sup>5</sup>) determination of gas-phase acidity of methanol. The three newer experimental results (Osborn *et al.*,<sup>3</sup> Dertinger *et al.*,<sup>4</sup> and DeTuri and Ervin<sup>5</sup>), as well as the very high-level theoretical study of Petraco *et al.*,<sup>12</sup> appear to sufficiently overlap between their mutual uncertainties, and, as a group, correspond to values that are generally higher than those selected by previous reviews and evaluations.<sup>13–24</sup> It is also interesting to note that most listed calculations<sup>6–9,11</sup> tend to predict values that are higher than earlier evaluations. On the other hand, the high-level W1 calculation (Parthiban and Martin<sup>10</sup>) predicts a somewhat lower value for the enthalpy of formation, closer to those recommended previously.<sup>13–24</sup> At the same time, it should be kept in mind that the measurements of Osborn *et al.*<sup>3</sup> and Dertinger *et al.*,<sup>4</sup> although quite convincing, by their nature technically correspond to upper limits. The slightly lower value based on the measurement of gas-phase acidity of methanol by DeTuri and Ervin,<sup>5</sup> while subject to a rather complex fitting and interpretation of data, is based on determining a threshold difference to a higher (HF) as well as a lower (H<sub>2</sub>O) acidity; the sum of the two threshold differences (79.6 kJ mol<sup>-1</sup>) agrees reasonably well (to ±2 kJ mol<sup>-1</sup>) with the difference between the two benchmark acidities (77.6 kJ mol<sup>-1</sup>). It should be also clearly noted that, in order to derive Δ<sub>f</sub>H°(CH<sub>3</sub>O), the three newer experimental values rely on different auxiliary thermochemical values [Δ<sub>f</sub>H°(CH<sub>3</sub>), Δ<sub>f</sub>H°(H<sub>2</sub>CO), Δ<sub>f</sub>H°(CH<sub>3</sub>OH)]; possible slight inconsistencies between these auxiliary values may additionally amplify the differences in the individual results inferred from those measurements.

In view of the discussion above, it is difficult to justify preference for any one particular experimental measurement. A linear analysis of all five listed experimental determina-

tions shows that the values in the set are in general agreement within their uncertainties, with the exception of the result based on the gas-phase acidity determination by Meot-Ner and Sieck.<sup>2</sup> The analysis shows that the latter measurement deviates consistently from all others significantly more than its original uncertainty of ±1.1 kJ mol<sup>-1</sup> would suggest, and that reconciliation with the other data can be achieved only if an amplified uncertainty of ±5.7 kJ mol<sup>-1</sup> is assumed.

The preferred value is the weighted average of all listed experimental measurements, taking into account the noted amplified uncertainty for the older gas-phase acidity determination.

The preferred value corresponds to the O–H bond dissociation energy in methanol  $D_{298}(\text{CH}_3\text{O}-\text{H}) = 440.0 \pm 2.2 \text{ kJ mol}^{-1}$  ( $434.6 \pm 2.2 \text{ kJ mol}^{-1}$  at 0 K) and the C–H bond dissociation energy in methoxy  $D_{298}(\text{H}-\text{CH}_2\text{O}) = 88.3 \pm 2.2 \text{ kJ mol}^{-1}$  ( $82.8 \pm 2.2 \text{ kJ mol}^{-1}$  at 0 K), which both produce the listed enthalpy when used together with auxiliary thermochemical values from Gurvich *et al.*<sup>16</sup>  $\Delta_f H^\circ_{298}(\text{CH}_3\text{OH}) = -201.0 \pm 0.6 \text{ kJ mol}^{-1}$ ,  $[H^\circ(298.15 \text{ K}) - H^\circ(0 \text{ K})](\text{CH}_3\text{OH}) = 11.441 \text{ kJ mol}^{-1}$ , (note that—without giving uncertainties—*TRC Thermochemical Tables*<sup>62</sup> list very similar values of  $\Delta_f H^\circ_{298}(\text{CH}_3\text{OH}) = -200.94 \text{ kJ mol}^{-1}$  and  $[H^\circ(298.15 \text{ K}) - H^\circ(0 \text{ K})](\text{CH}_3\text{OH}) = 11.440 \text{ kJ mol}^{-1}$ ),  $\Delta_f H^\circ_{298}(\text{CH}_2\text{O}) = -108.7 \pm 0.5 \text{ kJ mol}^{-1}$ ,  $[H^\circ(298.15 \text{ K}) - H^\circ(0 \text{ K})](\text{CH}_2\text{O}) = 10.020 \text{ kJ mol}^{-1}$ , and CODATA<sup>41</sup> recommended values  $\Delta_f H^\circ_{298}(\text{H}) = 217.998 \pm 0.006 \text{ kJ mol}^{-1}$ ,  $[H^\circ(298.15 \text{ K}) - H^\circ(0 \text{ K})](\text{H}) = 6.197 \pm 0.001 \text{ kJ mol}^{-1}$ ,  $[H^\circ(298.15 \text{ K}) - H^\circ(0 \text{ K})](\text{C, graphite}) = 1.050 \pm 0.020 \text{ kJ mol}^{-1}$ ,  $[H^\circ(298.15 \text{ K}) - H^\circ(0 \text{ K})](\text{H}_2) = 8.468 \pm 0.001 \text{ kJ mol}^{-1}$ , and  $[H^\circ(298.15 \text{ K}) - H^\circ(0 \text{ K})] \times (\text{O}_2) = 8.680 \pm 0.002 \text{ kJ mol}^{-1}$ , together with  $[H^\circ(298.15 \text{ K}) - H^\circ(0 \text{ K})](\text{CH}_3\text{O}) = 10.719 \text{ kJ mol}^{-1}$  as listed below.

Geometry (distance in Å, angles in degrees)<sup>(2a)</sup>

Z matrix						Cartesian coordinates				
						x	y	z		
C					C	0.0000	0.0000	-0.6740		
O	1	1.3926			O	0.0000	0.0000	0.7186		
H	1	1.1178	2	113.9	H	0.0000	1.0219	-1.1268		
H	1	1.1178	2	113.9	3	120	0.8850	-0.5110	-1.1268	
H	1	1.1178	2	113.9	3	-120	-0.8850	-0.5110	-1.1268	

Moments of inertia in the electronic ground state<sup>(2b)</sup>

$$I_A = 5.377 \times 10^{-47} \text{ kg m}^2$$

$$I_B = I_C = 30.045 \times 10^{-47} \text{ kg m}^2$$

Vibrational wave numbers in the electronic ground state  $\nu_i(\text{cm}^{-1})$ <sup>(2c)</sup>

2840 ( <i>a</i> <sub>1</sub> )	1412 ( <i>a</i> <sub>1</sub> )	1047 ( <i>a</i> <sub>1</sub> )	2778 ( <i>e</i> )
914 [ <i>A</i> <sub>1</sub> ] <sup>a</sup>	1465 [ <i>E</i> ] <sup>a</sup>	651.5 [ <i>A</i> <sub>1</sub> ] <sup>b</sup>	1210 [ <i>E</i> ] <sup>b</sup>

<sup>a,b</sup>Jahn–Teller split components of a nominally doubly degenerate vibrational mode.

Heat Capacity  $C_p^\circ$ , Entropy  $S^\circ$ , and Enthalpy Increment  $[H^\circ(T) - H^\circ(0\text{ K})]^{(2d),(2e)}$ 

T(K)	$C_p^\circ(T)$ ( $\text{J K}^{-1} \text{mol}^{-1}$ )	$S^\circ(T)$ ( $\text{J K}^{-1} \text{mol}^{-1}$ )	$[H^\circ(T) - H^\circ(0\text{ K})]$ ( $\text{kJ mol}^{-1}$ )
150	34.426	208.638	5.121
200	36.161	218.748	6.880
250	39.045	227.109	8.756
298.15	42.541	234.278	10.719
300	42.683	234.542	10.798
350	46.663	241.417	13.031
400	50.669	247.912	15.464
500	58.126	260.036	20.912
600	64.556	271.218	27.055
800	74.722	291.259	41.036
1000	82.197	308.777	56.765
1200	87.717	324.276	73.784
1500	93.451	344.513	101.022
2000	98.992	372.244	149.285
2500	101.975	394.685	199.597
3000	103.726	413.446	251.058

## 7-Constant NASA Polynomial

```
METHOXYL RADICAL JUN03 C 1.H 3.O 1. 0.G 200.000 6000.000 31.03392 1
0.47577924E+01 0.74414247E-02-0.26970518E-05 0.43809050E-09-0.26353710E-13 2
0.37811194E+03-0.19668003E+01 0.37118050E+01-0.28046331E-02 0.37655097E-04 3
-0.47307209E-07 0.18658842E-10 0.12956976E+04 0.65724086E+01 0.25257166E+04 4
```

## 9-Constant NASA Polynomial

```
METHOXYL RADICAL IUPAC Task Group on Selected Radicals
3 JUN03 C 1.00H 3.00O 1.00 0.00 0.00 0 31.03392 21000.000
50.000 200.0007 -2.0 -1.0 0.0 1.0 2.0 3.0 4.0 0.0 10718.970
0.191097376D+01-0.696218244D+01 0.455352324D+01-0.582817708D-02 0.875781412D-05
0.125622609D-06-0.223827550D-09 0.000000000D+00 0.124760229D+04 0.289376570D+01
200.000 1000.0007 -2.0 -1.0 0.0 1.0 2.0 3.0 4.0 0.0 10718.970
-0.105751911D+06 0.213849335D+04-0.121554327D+02 0.534065523D-01-0.633381272D-04
0.408392950D-07-0.109012101D-10 0.000000000D+00-0.827883262D+04 0.905643634D+02
1000.000 6000.0007 -2.0 -1.0 0.0 1.0 2.0 3.0 4.0 0.0 10718.970
0.184588307D+07-0.874640053D+04 0.182422790D+02-0.176462950D-02 0.340180180D-06
-0.349779939D-10 0.148446156D-14 0.000000000D+00 0.528627916D+05-0.950935544D+02
```

## Comments on Molecular Data, Heat Capacity, Entropy, and Enthalpy Increment

(2a) The structural data (Z-matrix and Cartesian coordinates) correspond to the experimentally assumed  $C_{3v}$  geometry and are based on Momose *et al.*,<sup>63</sup> who report  $r_{\text{CO}} = 1.39258 \pm 0.00022 \text{ \AA}$ ,  $r_{\text{CH}} = 1.11776 \pm 0.00046 \text{ \AA}$ , and  $\angle_{\text{HCO}} = 113.9^\circ \pm 1.8^\circ$ . The listed geometry results in rotational constants that are very similar to those listed in (2b):  $A = 5.339 \text{ cm}^{-1}$  and  $B = C = 0.881 \text{ cm}^{-1}$ , or  $I_A = 5.243 \times 10^{-47} \text{ kg m}^2$ ,  $I_B = I_C = 31.76 \times 10^{-47} \text{ kg m}^2$ . Note that Liu *et al.*,<sup>64</sup> who are the basis for the rotational constants listed by Jacox<sup>65</sup> and adopted here, report  $r_{\text{CO}} = 1.37 \pm 0.02 \text{ \AA}$ ,  $r_{\text{CH}} = 1.10 \pm 0.02 \text{ \AA}$ , and  $\angle_{\text{HCH}} = 109^\circ \pm 3^\circ$  (equivalent to  $\angle_{\text{HCO}} = 110^\circ \pm 3^\circ$ ). Note that the actual structure of  $\text{CH}_3\text{O}$  is slightly distorted by competing Jahn–Teller effect and spin–orbit splitting. Also note that standard electronic structure computations are able to implicitly treat the Jahn–Teller dis-

ortion, but not the spin–orbit effect, and, as a result, tend to optimize to a somewhat exaggeratedly distorted structure.

(2b) The listed moments of inertia correspond to experimental rotational constants<sup>64,65</sup>  $A_0 = 5.2059 \text{ cm}^{-1}$  and  $B_0 = C_0 = 0.9317 \text{ cm}^{-1}$ , which were used in the calculations of thermochemical functions.

(2c) The vibrational wavenumbers are experimental values tabulated by Jacox.<sup>65</sup> Note that the ground state of methoxy radical,  $\tilde{X}^2E$ , is subject to spin–orbit and Jahn–Teller effects and splits into two components:  $^2E_{3/2}$  and  $^2E_{1/2}$ , separated<sup>65</sup> by  $A = -61.97 \text{ cm}^{-1}$ . At the same time the doubly degenerate vibrational modes split into three components,  $E$ ,  $A_1$ , and  $A_2$ . Jacox<sup>65</sup> lists the  $E$  and  $A_1$  components for  $\nu_5$  and  $\nu_6$  as  $914 \text{ cm}^{-1}$  ( $A_1$ ),  $1465 \text{ cm}^{-1}$  ( $E$ ) and  $651.5 \text{ cm}^{-1}$  ( $A_1$ ),  $1210 \text{ cm}^{-1}$  ( $E$ ).

(2d) The heat capacities, integrated heat capacities and entropies were calculated in the rigid rotor-harmonic oscillator

approximation as explained below. In order to properly treat the splitting of the ground electronic state into two components as well as the competing splitting present in the two softer doubly degenerate vibrational modes  $\nu_5$  and  $\nu_6$  within the rigid rotor-harmonic oscillator framework, the contributions to the thermochemical functions were calculated in two separate steps and then added. The first part was calculated by treating the ground electronic state as two electronic components,  ${}^2E_{3/2}$ ,  $T_0=0$ ,  $g=3$ , and  ${}^2E_{3/2}$ ,  $T_0=61.97\text{ cm}^{-1}$ ,  $g=1$ . This part included the rotational contributions as well as vibrational contributions from the three singly degenerate vibrational modes,  $\nu_1-\nu_3$  (2840, 1412, and  $1047\text{ cm}^{-1}$ ), and the degenerate mode  $\nu_4$  of  $2778\text{ cm}^{-1}$ . The rotational constants and the vibrational wavenumbers corresponding to  $\nu_1-\nu_4$  were kept the same in both electronic components. The contributions arising from the doubly degenerate modes  $\nu_5$  and  $\nu_6$  were treated separately using the following approach: the  $A_1$ ,  $A_2$ , and  $E$  components were distributed into four pairs,  $\{\nu_5(A_1, A_2), \nu_6(E)\}$ ,  $\{\nu_5(E), \nu_6(A_1, A_2)\}$ ,  $\{\nu_5(A_1, A_2), \nu_6(A_1, A_2)\}$ , and  $\{\nu_5(E), \nu_6(E)\}$ . The (unknown) values of the  $A_2$  components were approximated by using the associated  $A_1$  components. Each of these four pairwise combinations was associated to one of the possible four components of a nominally unsplit  ${}^2E$  ground state (each electronic component having  $g=1$ ,  $T_0=0$ ). The vibrational contribution was then extracted and added to the contributions calculated in the first step. While it is readily recognized that this approach falls short of an accurate description of the actual spectroscopy of methoxy radical, it is felt that the approximations that were used here are reasonable within the rigid rotor-harmonic oscillator framework.

(2e) The standard heat capacity, entropy, and enthalpy increment values reported in the compilation of Gurvich *et al.*<sup>16</sup> are  $C_p^\circ(298.15\text{ K})=37.151\text{ J K}^{-1}\text{ mol}^{-1}$ ,  $S^\circ(298.15\text{ K})=232.861\text{ J K}^{-1}\text{ mol}^{-1}$ ,  $H^\circ(298.15\text{ K})-H^\circ(0\text{ K})=10.113\text{ kJ mol}^{-1}$ , in the *Thermochemical Database for Combustion*<sup>22</sup> are  $C_p^\circ(298.15\text{ K})=43.512\text{ J K}^{-1}\text{ mol}^{-1}$ ,  $S^\circ(298.15\text{ K})=229.390\text{ J K}^{-1}\text{ mol}^{-1}$ , and those obtained from G3MP2B3 computations<sup>11</sup> are  $C_p^\circ(298.15\text{ K})=41.07\text{ J K}^{-1}\text{ mol}^{-1}$ ,  $S^\circ(298.15\text{ K})=237.03\text{ J K}^{-1}\text{ mol}^{-1}$ ,  $H^\circ(298.15\text{ K})-H^\circ(0\text{ K})=10.44\text{ kJ mol}^{-1}$ .

## References

- J. L. Holmes and F. P. Lossing, *Int. J. Mass. Spectrom.* **58**, 113 (1984).
- M. Meot-Ner (Mautner) and L. W. Sieck, *J. Phys. Chem.* **90**, 6687 (1986).
- D. L. Osborn, D. J. Leahy, E. M. Ross, and D. M. Neumark, *Chem. Phys. Lett.* **235**, 484 (1995).
- S. Dertinger, A. Geers, J. Kappert, J. Wiebrecht, and F. Temps, *Faraday Discuss.* **102**, 31 (1995).
- V. F. DeTuri and K. M. Ervin, *J. Phys. Chem. A* **103**, 6911 (1999).
- C. W. Bauschlicher, Jr., S. R. Langhoff, and S. P. Walch, *J. Chem. Phys.* **96**, 450 (1992).
- M. R. Zachariah, P. R. Westmoreland, D. R. Burgess, Jr., W. Tsang, and C. F. Melius, *J. Phys. Chem.* **100**, 8737 (1996); see also D. R. F. Burgess, Jr., M. R. Zachariah, W. Tsang, and P. R. Westmoreland, *Prog. Energy Combust. Sci.* **21**, 453 (1995).
- L. A. Curtiss, K. Raghavachari, P. C. Redfern, and B. B. Stefanov, *J. Chem. Phys.* **108**, 692 (1998).
- L. A. Curtiss, K. Raghavachari, P. C. Redfern, V. Rassolov, and J. A. Pople, *J. Chem. Phys.* **109**, 7764 (1998).
- S. Parthiban and J. M. L. Martin (unpublished results, 2002).
- R. Janoschek and M. J. Rossi, *Int. J. Chem. Kinet.* **34**, 550 (2002).
- N. D. K. Petraco, W. D. Allen, and H. F. Schaefer III, *J. Chem. Phys.* **116**, 10229 (2002).
- D. F. McMillen and D. M. Golden, *Ann. Rev. Phys. Chem.* **33**, 493 (1982).
- L. Batt, *Int. Rev. Phys. Chem.* **6**, 53 (1987).
- B. Ruscic and J. Berkowitz, *J. Chem. Phys.* **95**, 4033 (1991).
- L. V. Gurvich, I. V. Veyts, and C. B. Alcock, *Thermodynamic Properties of Individual Substances*, 4th ed. (Hemisphere, New York, 1991), Vol. 2.
- S.-C. Kuo, Z. Zhang, R. B. Klemm, J. F. Liebman, L. J. Stief, and F. L. Nesbitt, *J. Phys. Chem.* **98**, 4026 (1994).
- J. Berkowitz, G. B. Ellison, and D. Gutman, *J. Phys. Chem.* **98**, 2744 (1994).
- Computational Chemistry Comparison and Benchmark DataBase (CCCBDB) (NIST, 1999); see <http://srdata.nist.gov/cccbdb/>
- R. Atkinson, D. L. Baulch, R. A. Cox, R. F. Hampson, Jr., J. A. Kerr, M. J. Rossi, and J. Troe, *J. Phys. Chem. Ref. Data* **29**, 167 (2000).
- J. A. Kerr and D. W. Stocker, *Strengths of Chemical Bonds*, in *CRC Handbook of Chemistry and Physics*, edited by D. Lide, 82nd ed. (CRC, Boca Raton, FL, 2001–2002).
- A. Burcat, TAE Report No. 867, Technion, Haifa, 2001; see also <ftp://ftp.technion.ac.il/pub/supported/aetdd/thermodynamics>
- S. P. Sander, R. R. Friedl, D. M. Golden, M. J. Kurylo, R. E. Huie, V. L. Orkin, G. K. Moortgat, A. R. Ravishankara, C. E. Kolb, M. J. Molina, and B. J. Finlayson-Pitts, JPL Publication 02–25, NASA and JPL, February 1, 2003.
- H. Y. Afeefy, J. F. Liebman, and S. E. Stein, *Neutral Thermochemical Data*, in *NIST Chemistry WebBook*, NIST Standard Reference Database Number 69, edited by P. J. Linstrom and W. G. Mallard (NIST, Gaithersburg, MD, 2003); <http://webbook.nist.gov/>
- F. P. Lossing, *J. Am. Chem. Soc.* **99**, 7526 (1977).
- B. Ruscic, A. F. Wagner, L. B. Harding, R. L. Asher, D. Feller, D. A. Dixon, K. A. Peterson, Y. Song, X. Qian, C.-Y. Ng, J. Liu, W. Chen, and D. W. Schwenke, *J. Phys. Chem. A* **106**, 2727 (2002).
- L. V. Gurvich, I. V. Veyts, and C. B. Alcock, *Thermodynamic Properties of Individual Substances*, 4th ed. (Hemisphere, New York, 1989), Vol. 1.
- B. Ruscic (unpublished results, 2003).
- T. M. Ramond, G. E. Davico, R. L. Schwartz, and W. C. Lineberger, *J. Chem. Phys.* **112**, 1158 (2000).
- G. W. Erickson, *J. Phys. Chem. Ref. Data* **6**, 831 (1977).
- D. L. Osborn, D. J. Leahy, E. H. Kim, E. de Beer, and D. M. Neumark, *Chem. Phys.* **292**, 651 (1998).
- M. W. Chase, Jr., C. A. Davies, J. R. Downey, Jr., D. J. Frurip, R. A. McDonald, and A. N. Syverud, *JANAF Thermochemical Tables*, 3rd ed., *J. Phys. Chem. Ref. Data* **14**, Suppl. 1 (1985).
- M. W. Chase, Jr., *NIST-JANAF Thermochemical Tables*, 4th ed., *J. Phys. Chem. Ref. Data Monogr.* **9** (1998).
- K. M. Ervin and V. F. DeTuri, *J. Phys. Chem. A* **106**, 9947 (2002).
- F. Caralp, M.-T. Rayez, W. Forst, N. Gomez, B. Delcroix, C. Fittschen, and P. Devolder, *J. Chem. Soc. Faraday Trans.* **94**, 3321 (1998).
- L. A. Curtiss, P. C. Redfern, K. Raghavachari, V. Rassolov, and J. A. Pople, *J. Chem. Phys.* **110**, 4703 (1999).
- L. A. Curtiss, K. Raghavachari, P. C. Redfern, and J. A. Pople, *J. Chem. Phys.* **106**, 1063 (1997); see also L. A. Curtiss, L. D. Kock, and J. A. Pople, *ibid.* **95**, 4040 (1991).
- S. Parthiban and J. M. L. Martin, *J. Chem. Phys.* **114**, 6014 (2001).
- A. G. Baboul, L. A. Curtiss, P. C. Redfern, and K. Raghavachari, *J. Chem. Phys.* **110**, 7650 (1999).
- L. Batt, K. Christie, R. T. Milne, and A. J. Summers, *Int. J. Chem. Kinet.* **6**, 877 (1974).
- J. D. Cox, D. D. Wagman, and V. A. Medvedev, *CODATA Key Values for Thermodynamics* (Hemisphere, New York, 1989); see also <http://www.codata.org/codata/databases/key1.html>
- L. Batt, K. Christie, R. T. Milne, and A. J. Summers, *Int. J. Chem. Kinet.* **6**, 877 (1974); L. Batt and R. T. Milne, *ibid.* **6**, 945 (1974).
- L. Batt and R. D. McCulloch, *Int. J. Chem. Kinet.* **8**, 491 (1976).
- F. O. Rice and W. R. Johnston, *J. Am. Chem. Soc.* **56**, 214 (1934).
- S. W. Benson, *J. Chem. Phys.* **40**, 1007 (1964).



- <sup>46</sup>S. W. Benson and K. H. Anderson, *J. Chem. Phys.* **39**, 1671 (1963).
- <sup>47</sup>J. Takezaki and C. Takeuchi, *J. Chem. Phys.* **22**, 1527 (1954).
- <sup>48</sup>P. L. Hanst and J. G. Calvert, *J. Phys. Chem.* **63**, 104 (1959).
- <sup>49</sup>P. Gray, *Trans. Faraday Soc.* **52**, 344 (1956).
- <sup>50</sup>E. W. R. Steacie and D. S. Calder, *J. Chem. Phys.* **4**, 96 (1934).
- <sup>51</sup>A. Appin, Ju. Chariton, and O. Todes, *Acta Physicochim. USSR* **5**, 655 (1936).
- <sup>52</sup>R. H. Martin, F. W. Lampe, and R. W. Taft, *J. Am. Chem. Soc.* **88**, 1353 (1966).
- <sup>53</sup>M. A. Haney and J. L. Franklin, *Trans. Faraday Soc.* **65**, 1794 (1969).
- <sup>54</sup>S. Tsuda and W. H. Hamil, *Adv. Mass Spectrom.* **3**, 249 (1966).
- <sup>55</sup>V. P. Glushko, L. V. Gurvich, G. A. Bergman, I. V. Veits, V. A. Medvedev, G. A. Khackhuruzov, and V. S. Yungman, *Termodinamicheski Svoistva Individual'nikh Veschestv*, 3rd ed. (Nauka, Moscow, 1979).
- <sup>56</sup>L. Batt, J. P. Burrows, and G. N. Robinson, *Chem. Phys. Lett.* **78**, 467 (1981).
- <sup>57</sup>J. C. Traeger and J. L. Holmes, *J. Phys. Chem.* **97**, 3453 (1993).
- <sup>58</sup>P. C. Engelking, G. B. Ellison, and W. C. Lineberger, *J. Chem. Phys.* **69**, 1826 (1978).
- <sup>59</sup>A. Burcat and S. A. Kudchadker, *Acta Chim. Hungar.* **101**, 249 (1979).
- <sup>60</sup>W. Tsang, *Heats of Formation of Organic Free Radicals by Kinetic Methods*, in *Energetics of Organic Free Radicals*, edited by J. A. M. Simoes, A. Greenberg, and J. F. Liebman, Structure, Energetics and Reactivity in Chemistry (SEARCH) Series (Chapman and Hall, London, 1996).
- <sup>61</sup>W. B. DeMore, S. P. Sander, D. M. Golden, R. F. Hampson, M. J. Kurylo, C. J. Howard, A. R. Ravishankara, C. E. Kolb, and M. J. Molina, Evaluation No. 12, JPL Publication 97-4, NASA and JPL, January 15, 1997.
- <sup>62</sup>*TRC Thermodynamic Tables—Nonhydrocarbons* (Texas A and M University System, December 31, 1986).
- <sup>63</sup>T. Momose, Y. Endo, E. Hirota, and T. Shida, *J. Chem. Phys.* **88**, 5338 (1988).
- <sup>64</sup>X. Liu, C. P. Damo, T.-Y. D. Lin, S. C. Foster, P. Misra, L. Yu, and T. A. Miller, *J. Phys. Chem.* **93**, 2266 (1989).
- <sup>65</sup>M. E. Jacox, *J. Phys. Chem. Ref. Data* **32**, 1 (2003).

7.3.3. CH<sub>3</sub>CH<sub>2</sub>O Radical

2154-50-9

## 7.3.3. Ethoxyl radical

CH <sub>3</sub> CH <sub>2</sub> O( <sup>2</sup> A'')	C <sub>2v</sub> (σ <sub>ext</sub> =2)
Δ <sub>f</sub> H°(298.15 K) = -13.6 ± 4.0 kJ mol <sup>-1</sup>	Δ <sub>f</sub> H°(0 K) = -0.2 ± 4.0 kJ mol <sup>-1</sup>
C° <sub>p</sub> (298.15 K) = 66.321 J K <sup>-1</sup> mol <sup>-1</sup>	H°(298.15 K) - H°(0 K) = 14.235 kJ mol <sup>-1</sup>
S°(298.15 K) = 277.642 J K <sup>-1</sup> mol <sup>-1</sup>	p° = 100 000 Pa (1 bar)

## Literature Data for the Enthalpy of Formation at 298.15 K

Δ <sub>f</sub> H°/kJ mol <sup>-1</sup>	Authors and Reference	Method <sup>a</sup>	Comments
<b>Measurements</b>			
-13.6 <sup>b</sup> ± 4.0 <sup>c</sup>	DeTuri and Ervin (1999) <sup>1</sup>	TCID-NIC	(1a)
<b>Computations</b>			
-7.5 ± 13 <sup>c</sup>	Curtiss <i>et al.</i> (1998) <sup>2</sup>	CBS-Q	(1b)
-10.5 ± 7.9 <sup>c</sup>	Curtiss <i>et al.</i> (1998) <sup>3</sup>	G3	(1c)
0 ± 6 <sup>c</sup>	Caralp <i>et al.</i> (1999) <sup>4</sup>	QCISD(T), BAC-MP4	(1d)
-9.0 <sup>b</sup> ± 10 <sup>c</sup>	Yamada <i>et al.</i> (1999) <sup>5</sup>	CBS-q, G2	(1e)
-12.1 ± 3.1 <sup>c</sup>	Parthiban and Martin (2001) <sup>6</sup>	W1	(1f)
-16.4 ± 7.8	Janoschek and Rossi (2002) <sup>7</sup>	G3MP2B3	(1g)
<b>Reviews and Evaluations</b>			
-17.2 ± 4.2	McMillen and Golden (1982) <sup>8</sup>	CDE	(1h)
-16.6	Batt (1987) <sup>9</sup>	CDE	(1i)
-15.5 ± 3.3	Berkowitz <i>et al.</i> (1994) <sup>10</sup>	CDE	(1j)
-15.5 ± 3.4	Atkinson <i>et al.</i> (2000) <sup>11</sup>	TT-A	(1k)
-15.5 ± 3.4	Kerr and Stocker (2000) <sup>12</sup>	TT-A	(1l)
-16.7	Burcat (2001) <sup>13</sup>	TT-A	(1m)
-15.5 ± 3.3	Sander <i>et al.</i> (2003) <sup>14</sup>	TT-A	(1n)

<sup>a</sup>TCID-NIC: negative ion cycle based on combining energy-resolved threshold collision-induced dissociation measurements of proton-bound complex with electron affinity of the hydrocarbon radical from negative ion photoelectron spectroscopy; CDE: critical data evaluation; and TT-A: annotated tabulation of thermodynamic data.

<sup>b</sup>The quoted value was either not given explicitly by the author(s) or it was recalculated using auxiliary thermochemical values that differ from those used by the original authors; see individual comments for additional details.

<sup>c</sup>The uncertainty was either not given explicitly by the original author(s) or it has been modified; see individual comments for further explanations.

## Comments on the Enthalpies of Formation

(1a) Gas-phase acidity of ethanol from energy-resolved TCID measurements of the fluoride-ethanol, ethoxide-water, and ethoxide-ethanol proton-bound complexes. The competitive dissociation reactions of the complexes were studied using a guided ion beam tandem mass spectrometer, where the reaction cross sections and product branching fractions to the two proton transfer channels were measured as a function of collision energy. From the RRKM-modeled enthalpy difference between the product channels, the gas-phase acidity of Δ<sub>acid</sub>H°<sub>0</sub>(CH<sub>3</sub>CH<sub>2</sub>OH) = 1581 ± 5 kJ mol<sup>-1</sup> was determined. In light of a change in the gas-phase acidity of water by Ruscic *et al.*,<sup>15</sup> this value was subsequently revised downward by Ervin and DeTuri<sup>16</sup> to 1579.8 ± 3.1 kJ mol<sup>-1</sup>. Using the electron affinity E<sub>ea</sub>(CH<sub>3</sub>CH<sub>2</sub>O) = 1.712 ± 0.004 eV from Ramond *et al.*<sup>17</sup> and the ionization energy E<sub>i</sub>(H)/hc = 109 678.773 704 ± 0.000 006 cm<sup>-1</sup> from Erickson<sup>18</sup> produces D<sub>0</sub>(CH<sub>3</sub>CH<sub>2</sub>O-H) = 432.9 ± 3.1 kJ mol<sup>-1</sup>. With auxiliary quantities [H°(298.15 K) - H°(0 K)](CH<sub>3</sub>CH<sub>2</sub>OH) = 14.126 kJ mol<sup>-1</sup> and Δ<sub>f</sub>H°<sub>298</sub>(CH<sub>3</sub>CH<sub>2</sub>OH) = -234.8 ± 0.5 kJ mol<sup>-1</sup> from Gurvich *et al.*,<sup>19</sup> [H°(298.15 K) - H°(0 K)](H)

= 6.197 kJ mol<sup>-1</sup> and Δ<sub>f</sub>H°<sub>298</sub>(H) = 217.998 ± 0.006 kJ mol<sup>-1</sup> as recommended by CODATA,<sup>20</sup> and the currently adopted enthalpy increment for ethoxyl, [H°(298.15 K) - H°(0 K)](CH<sub>3</sub>CH<sub>2</sub>O) = 14.235 kJ mol<sup>-1</sup>, this produces D<sub>298</sub>(CH<sub>3</sub>CH<sub>2</sub>O-H) = 439.2 ± 3.1 kJ mol<sup>-1</sup> and Δ<sub>f</sub>H°<sub>298</sub>(CH<sub>3</sub>CH<sub>2</sub>O) = -13.6 ± 3.1 kJ mol<sup>-1</sup>. Apart from the uncertainty, this is the value listed in the table. Note that Ervin and DeTuri<sup>16</sup> starting from their Δ<sub>acid</sub>H°<sub>298</sub> obtain the same value for D<sub>0</sub>, but their D<sub>298</sub> is slightly lower: 438.1 ± 3.3 kJ mol<sup>-1</sup>, most likely due to the use of a lower enthalpy increment for ethoxyl. These differences are further amplified by using Δ<sub>f</sub>H°<sub>298</sub>(CH<sub>3</sub>CH<sub>2</sub>OH) = -235.3 ± 0.5 kJ mol<sup>-1</sup> as suggested by the WebBook,<sup>21</sup> resulting in an enthalpy of formation of ethoxyl at 298.15 K of -15.1 ± 3.3 kJ mol<sup>-1</sup>. Noting that the underlying treatment of the partition functions probably affects the fitted thresholds to some degree, we here adopt a slightly amplified uncertainty of ± 4 kJ mol<sup>-1</sup>.

(1b) CBS-Q calculation. The reported average absolute deviation of 1.57 kcal mol<sup>-1</sup> was multiplied by 2 to bring it closer to the desired 95% confidence limit. The equivalent CBS-q and CBS-4 enthalpies of formation are -2.1

$\pm 18 \text{ kJ mol}^{-1}$  ( $-0.5 \text{ kcal mol}^{-1}$ ) and  $-7.5 \pm 26 \text{ kJ mol}^{-1}$  ( $-1.8 \text{ kcal mol}^{-1}$ ), where the uncertainties have been obtained in an analogous way.

(1c) G3 *ab initio* calculation. The value listed in the table is converted from  $-2.5 \text{ kcal mol}^{-1}$ . The uncertainty quoted in the table corresponds approximately to 95% confidence limits, based on twice the average absolute deviation of  $0.94 \text{ kcal mol}^{-1}$  for the enthalpies in the G2/97 test set, which roughly corresponds to 1 s.d. At the G3(MP2) level of theory<sup>22</sup>  $\Delta_f H^\circ_{298}(\text{CH}_3\text{CH}_2\text{O}) = -8.4 \pm 9.9^\circ \text{ kJ mol}^{-1}$  ( $-2.0 \text{ kcal mol}^{-1}$ ), where the quoted uncertainty has been derived in a similar fashion as for the G3 value. At the G2 level of theory<sup>23</sup>  $\Delta_f H^\circ_{298}(\text{CH}_3\text{CH}_2\text{O}) = -9.6 \pm 13.1 \text{ kJ mol}^{-1}$  ( $-2.3 \text{ kcal mol}^{-1}$ ).

(1d) QCISD(T) and BAC-MP4 calculations accompanying an experimental kinetic study of thermal decomposition of ethoxyl radicals. The C–C and C–H bond dissociation energies in the ethoxy radical are calculated using various levels of theory. The results obtained at the QCISD(T)/6-311+G(3df,2p)//MP2/6-311G(d,p) and BAC-MP4 theoretical levels are close to each other and are hence believed by the authors to be the most reliable ones:  $D_{298}(\text{CH}_3\text{--CH}_2\text{O}) = 39.7$  and  $40.2 \text{ kJ mol}^{-1}$  and  $D_{298}(\text{CH}_3\text{CH}(\text{O})\text{--H}) = 55.1$  and  $58.8 \text{ kJ mol}^{-1}$ . Combining the calculated bond dissociation energies with the enthalpies of formation of  $\Delta_f H^\circ_{298}(\text{CH}_3) = 145.7 \text{ kJ mol}^{-1}$ ,<sup>10</sup>  $\Delta_f H^\circ_{298}(\text{CH}_2\text{O}) = -108.6 \text{ kJ mol}^{-1}$ ,<sup>24</sup>  $\Delta_f H^\circ_{298}(\text{H}) = 218.0 \text{ kJ mol}^{-1}$ ,<sup>25</sup> and  $\Delta_f H^\circ_{298}(\text{CH}_3\text{CHO}) = -166.1 \text{ kJ mol}^{-1}$ ,<sup>26</sup> the authors obtain  $\Delta_f H^\circ_{298}(\text{CH}_3\text{CH}_2\text{O}) = 0 \pm 3 \text{ kJ mol}^{-1}$ , and note that their result is significantly different from the recommended experimental value of  $-15.5 \text{ kJ mol}^{-1}$  of Berkowitz *et al.*<sup>10</sup> The uncertainty quoted by the authors ( $\pm 3 \text{ kJ mol}^{-1}$ ) seems to try to capture the difference between the two kinds of calculations employed and appears highly optimistic even when multiplied by a factor of 2.

(1e) The isodesmic reaction  $\text{CH}_3\text{CH}_2\text{O} + \text{CH}_3\text{OH} \rightarrow \text{CH}_3\text{CH}_2\text{OH} + \text{CH}_3\text{O}$  studied using CBS-q//MP2(full)/6-31G(d,p) and G2 methods. Total energies are corrected for zero-point vibrational energies and thermal corrections to 298.15 K are incorporated. [Frequencies are scaled by 0.9608 for MP2(full)/6-31G(d,p) and 0.8929 for HF/6-31G(d).] Using literature values of  $\Delta_f H^\circ_{298}$  for three other species,<sup>27,28</sup>  $\Delta_f H^\circ_{298}(\text{CH}_3\text{CH}_2\text{O}) = -7.0 \text{ kJ mol}^{-1}$  and  $\Delta_f H^\circ_{298}(\text{CH}_3\text{CH}_2\text{O}) = -14.0 \text{ kJ mol}^{-1}$  were obtained for the reaction enthalpies calculated by the CBS-q and G2 methods, respectively. The authors also note that their estimation of the stability of ethoxyl relative to  $\text{C}_2\text{H}_4 + \text{OH}$  is  $-99 \text{ kJ mol}^{-1}$ , from which one can infer that they prefer the G2 value, which is listed in the table. It should be noted, however, that the value for the enthalpy of ethoxyl is determined relative to the enthalpy of methoxyl, which was taken as  $16.0 \text{ kJ mol}^{-1}$  at 298.15 K based on the recommendation of Tsang and Hampson.<sup>29</sup> The currently recommended value for the enthalpy of ethoxyl is  $5 \text{ kJ mol}^{-1}$  higher.

(1f) W1 *ab initio* computation. The uncertainty quoted in the table corresponds approximately to 95% confidence limits based on twice the average absolute deviation of

$0.37 \text{ kcal mol}^{-1}$  for the W1 test set, which corresponds roughly to 1 s.d.

(1g) G3(MP2)//B3LYP *ab initio* calculations for 32 selected free radicals. The uncertainty given in the table corresponds approximately to 95% confidence limits based on twice the quoted average absolute deviation of  $3.9 \text{ kJ mol}^{-1}$  for the calculated set of radicals, which corresponds roughly to 1 s.d. Note that the average absolute deviation for all enthalpies in the G2/97 test set using the same method is very slightly larger:<sup>30</sup>  $4.7 \text{ kJ mol}^{-1}$  [see also (1c) above].

(1h) Recommended value from extensive evaluation of data (mainly kinetic determinations) published until 1981. The selected value is based on the kinetic determination by Batt *et al.*<sup>31</sup>

(1i) A review of kinetics and thermochemistry of alkoxy and alkyl peroxy radical reactions. The suggested thermochemical properties,  $\Delta_f H^\circ_{298}(\text{CH}_3\text{CH}_2\text{O}) = -16.6 \text{ kJ mol}^{-1}$  and  $D_{298}(\text{CH}_3\text{CH}_2\text{O--H}) = 436.2 \text{ kJ mol}^{-1}$ , obtained with the auxiliary data<sup>19,20</sup> of  $\Delta_f H^\circ_{298}(\text{CH}_3\text{CH}_2\text{OH}) = -234.8 \text{ kJ mol}^{-1}$  and  $\Delta_f H^\circ_{298}(\text{H}) = 217.998 \text{ kJ mol}^{-1}$ , are based on previous kinetic studies of diethyl peroxy and ethyl nitrate decomposition reactions.

(1j) Critical data evaluation of R–H bond dissociation energies based on three methods: kinetic determinations, positive ion cycle determinations from photoelectron/photoionization measurements and negative ion cycle determinations from photoelectron measurements of negative ions combined with gas phase acidities. The recommended value is based on the bond dissociation energy  $D_{298}(\text{CH}_3\text{CH}_2\text{O--H}) = 437.6 \pm 3.3 \text{ kJ mol}^{-1}$  reported by Ervin *et al.*,<sup>32</sup> which is based on a redetermination of the gas-phase acidity of acetylene and literature values for relative gas-phase acidities of alcohols.

(1k) Critical evaluation of atmospherically relevant kinetic rates. Their table of enthalpy data lists Kerr and Stocker<sup>12</sup> [see (1l) below] as the source, who in turn adopt the recommendation of Berkowitz *et al.*<sup>10</sup> [see (1j) above].

(1l) Thermodynamic data compilation. The tabulation selects  $D_{298}(\text{CH}_3\text{CH}_2\text{O--H}) = 436.0 \pm 3.8 \text{ kJ mol}^{-1}$  citing Berkowitz *et al.*<sup>10</sup> [see (1j) above] as a source.

(1m) Thermodynamic database for combustion. Burcat quotes Benson<sup>33</sup> as the source of  $\Delta_f H^\circ_{298}(\text{CH}_3\text{CH}_2\text{O})$ .

(1n) Critical evaluation of atmospherically relevant kinetic data. The quoted value is from Berkowitz *et al.*<sup>10</sup> [see (1j) above].

### Preferred Value of the Enthalpy of Formation

$$\Delta_f H^\circ(298.15 \text{ K}) = -13.6 \pm 4.0 \text{ kJ mol}^{-1}$$

$$\Delta_f H^\circ(0 \text{ K}) = -0.2 \pm 4.0 \text{ kJ mol}^{-1}$$

The only new experimental enthalpy of formation determined since 1982, the publication of the review by McMillen and Golden,<sup>8</sup> is that reported by DeTuri and Ervin.<sup>1</sup> Another experimentally based value, derived from earlier measurements, was reported by Batt.<sup>9</sup> The experimental values are, however, definitely lower than the results of *ab initio* calculations. Omitting the high value reported by Caralp *et al.*<sup>4</sup>

[see (1d) above], which appears incompatible with all other listed calculations, the average theoretical enthalpy of formation is  $\Delta_f H^\circ_{298}(\text{CH}_3\text{CH}_2\text{O}) = -11.6 \pm 1.7 \text{ kJ mol}^{-1}$ . It should be also noted that some of the listed computations do not use a hindered rotor approach to estimating the enthalpy increment needed to obtain the 298.15 K value, and none seem to include the low-lying excited electronic state of ethoxyl. If the enthalpy increment for ethoxyl adopted here were used, the reported results would be another  $1-2 \text{ kJ mol}^{-1}$  higher (less negative), further exacerbating the difference between the theoretical and experimental value. On the other hand, the best available calculation<sup>6</sup> (W1) produces one of the lowest calculated values, which—within the stated uncertainty—overlaps with the experimental value of DeTuri and Ervin,<sup>1</sup> even when the additional correction of  $1-2 \text{ kJ mol}^{-1}$  upwards is taken into account.

The preferred enthalpy of formation is the value based on the TCID measurements of DeTuri and Ervin<sup>1</sup> which lies between the theoretical results and previous recommendations. It is important to note that the preferred enthalpy results in an O–H bond dissociation energy in ethanol (see below) that is in line with the much better established O–H dissociation energy in methanol,  $D_{298}(\text{CH}_3\text{O–H}) = 440.0 \pm 2.2 \text{ kJ mol}^{-1}$  ( $434.6 \pm 2.2 \text{ kJ mol}^{-1}$  at 0 K), recom-

mended in the present evaluation. This lends additional support to the presently selected enthalpy of formation of ethoxyl radical.

The preferred value corresponds to the O–H bond dissociation energy in ethanol  $D_{298}(\text{CH}_3\text{CH}_2\text{O–H}) = 439.2 \pm 4.0 \text{ kJ mol}^{-1}$  ( $432.9 \pm 4.0 \text{ kJ mol}^{-1}$  at 0 K) and the C–C bond dissociation energy in ethoxy  $D_{298}(\text{CH}_3\text{–CH}_2\text{O}) = 51.6 \pm 4.0 \text{ kJ mol}^{-1}$  ( $45.4 \pm 4.0 \text{ kJ mol}^{-1}$  at 0 K), which both produce the listed enthalpy when used together with auxiliary thermochemical values from Gurvich *et al.*,<sup>19</sup>  $\Delta_f H^\circ_{298}(\text{CH}_3\text{CH}_2\text{OH}) = -234.8 \pm 0.5 \text{ kJ mol}^{-1}$ ,  $[H^\circ(298.15 \text{ K}) - H^\circ(0 \text{ K})](\text{CH}_3\text{CH}_2\text{OH}) = 14.126 \text{ kJ mol}^{-1}$ ,  $\Delta_f H^\circ_{298}(\text{CH}_2\text{O}) = -108.7 \pm 0.5 \text{ kJ mol}^{-1}$ ,  $[H^\circ(298.15 \text{ K}) - H^\circ(0 \text{ K})](\text{CH}_2\text{O}) = 10.020 \text{ kJ mol}^{-1}$ , and CODATA<sup>20</sup> recommended values  $\Delta_f H^\circ_{298}(\text{H}) = 217.998 \pm 0.006 \text{ kJ mol}^{-1}$ ,  $[H^\circ(298.15 \text{ K}) - H^\circ(0 \text{ K})](\text{H}) = 6.197 \pm 0.001 \text{ kJ mol}^{-1}$ ,  $[H^\circ(298.15 \text{ K}) - H^\circ(0 \text{ K})](\text{C, graphite}) = 1.050 \pm 0.020 \text{ kJ mol}^{-1}$ ,  $[H^\circ(298.15 \text{ K}) - H^\circ(0 \text{ K})](\text{H}_2) = 8.468 \pm 0.001 \text{ kJ mol}^{-1}$ , and  $[H^\circ(298.15 \text{ K}) - H^\circ(0 \text{ K})](\text{O}_2) = 8.680 \pm 0.002 \text{ kJ mol}^{-1}$ , together with  $[H^\circ(298.15 \text{ K}) - H^\circ(0 \text{ K})](\text{CH}_3\text{CH}_2\text{O}) = 14.235 \text{ kJ mol}^{-1}$  as listed below, and  $\Delta_f H^\circ_{298}(\text{CH}_3) = 146.7 \pm 0.3 \text{ kJ mol}^{-1}$ ,  $[H^\circ(298.15 \text{ K}) - H^\circ(0 \text{ K})](\text{CH}_3) = 10.366 \text{ kJ mol}^{-1}$  from the present compilation.

### Geometry (distance in Å, angles in degrees)<sup>(2a)</sup>

Z matrix							Cartesian coordinates						
							x	y	z				
C							C	-1.045 721	-0.600 479	0.000 000			
C	1	1.5283					C	0.000 000	0.514 051	0.000 000			
O	2	1.3709	1	115.521			O	1.306 329	0.098 280	0.000 000			
H	1	1.0965	2	110.999	3	180	H	-2.061 111	-0.186 582	0.000 000			
H	1	1.0950	2	110.394	3	59.749	H	-0.929 743	-1.232 536	0.886 587			
H	1	1.0950	2	110.394	3	-59.749	H	-0.929 743	-1.232 536	-0.886 587			
H	2	1.1100	1	111.505	4	57.353	H	-0.127 854	1.191 991	0.869 571			
H	2	1.1100	1	111.505	4	-57.353	H	-0.127 854	1.191 991	-0.869 571			
Moments of inertia in the electronic ground state <sup>(2b)</sup>													
$I_A = 21.281 \times 10^{-47} \text{ kg m}^2$							$I_B = 88.117 \times 10^{-47} \text{ kg m}^2$			$I_C = 99.060 \times 10^{-47} \text{ kg m}^2$			
							$I_r = 4.303 \times 10^{-47} \text{ kg m}^2$ ( $V_3 = 737 \text{ cm}^{-1}$ , $\sigma_{\text{int}} = 3$ )						
Vibrational wave numbers in the electronic ground state $\nu_i(\text{cm}^{-1})$ <sup>(2c)</sup>													
3015			3004		2937		2824		2790		1468		
1458			1378		1360		1321		1206		1064		
1046			872		856		475		406		220(torsion)		

### Excited Electronic States<sup>(2d)</sup>

Term value:  $T_0(\tilde{A}^2 A') = 355 \pm 10 \text{ cm}^{-1}$  ( $C_s, \sigma_{\text{ext}} = 1$ )

Moments of Inertia:  $I_A = 23.996 \times 10^{-47} \text{ kg m}^2$ ,  $I_B = 81.338 \times 10^{-47} \text{ kg m}^2$ ,  $I_C = 94.591 \times 10^{-47} \text{ kg m}^2$ ,  $I_r = 4.375 \times 10^{-47} \text{ kg m}^2$  ( $V_3 = 1030 \text{ cm}^{-1}$ ,  $\sigma_{\text{int}} = 3$ )

Vibrational wave numbers  $\nu_i(\text{cm}^{-1})$ : 3028 ( $a'$ ), 2951 ( $a'$ ), 2850 ( $a'$ ), 1514 ( $a'$ ), 1471 ( $a'$ ), 1356 ( $a'$ ), 1268 ( $a'$ ), 1107 ( $a'$ ), 912 ( $a'$ ), 874 ( $a'$ ), 369 ( $a'$ ), 3040 ( $a''$ ), 2886 ( $a''$ ), 1445 ( $a''$ ), 1216 ( $a''$ ), 934 ( $a''$ ), 577 ( $a''$ ), 249 ( $a''$ , torsion)

Heat Capacity  $C_p^\circ$ , Entropy  $S^\circ$ , and Enthalpy Increment  $[H^\circ(T) - H^\circ(0\text{ K})]^{(2e),(2f)}$ 

$T/\text{K}$	$C_p^\circ(T)$ ( $\text{J K}^{-1}\text{ mol}^{-1}$ )	$S^\circ(T)$ ( $\text{J K}^{-1}\text{ mol}^{-1}$ )	$[H^\circ(T) - H^\circ(0\text{ K})]$ ( $\text{kJ mol}^{-1}$ )
150	48.062	239.016	5.753
200	54.390	253.730	8.318
250	60.352	266.506	11.187
298.15	66.321	277.642	14.235
300	66.556	278.053	14.358
350	72.975	288.794	17.846
400	79.362	298.957	21.655
500	91.301	317.974	30.200
600	101.740	335.566	39.864
800	118.609	367.259	61.979
1000	131.373	395.163	87.036
1200	141.034	420.010	114.321
1500	151.303	452.663	158.278
2000	161.468	497.737	236.739
2500	167.046	534.424	318.997
3000	170.359	565.197	403.414

## 7-Constant NASA Polynomial

```

ETHOXYL RADICAL  JUN03 C  2.H  5.0  1.  0.G  200.000  6000.000  45.06050  1
0.66889982E+01  0.13125676E-01-0.47038840E-05  0.75858552E-09-0.45413306E-13  2
-0.47457832E+04-0.96983755E+01  0.43074268E+01  0.64147205E-02  0.31139714E-04  3
-0.43314083E-07  0.17276184E-10-0.34027524E+04  0.59025837E+01-0.16357022E+04  4

```

## 9-Constant NASA Polynomial

```

ETHOXYL RADICAL  IUPAC Task Group on Selected Radicals
3 JUN03 C  2.00H  5.000  1.00  0.00  0.00  0  45.06050  -13600.000
50.000  200.0007 -2.0 -1.0  0.0  1.0  2.0  3.0  4.0  0.0  14235.043
-0.234929855D+04  0.146234655D+03  0.673498365D+00  0.253875617D-01  0.125848479D-03
-0.100421507D-05  0.194871527D-08  0.000000000D+00-0.383489634D+04  0.219541939D+02
200.000  1000.0007 -2.0 -1.0  0.0  1.0  2.0  3.0  4.0  0.0  14235.043
-0.227876925D+06  0.372743127D+04-0.194122340D+02  0.814283794D-01-0.929029798D-04
0.585878240D-07-0.154024440D-10  0.000000000D+00-0.207566010D+05  0.134580038D+03
1000.000  6000.0007 -2.0 -1.0  0.0  1.0  2.0  3.0  4.0  0.0  14235.043
0.379459991D+07-0.163151458D+05  0.308299459D+02-0.302045663D-02  0.563059677D-06
-0.562294840D-10  0.232626271D-14  0.000000000D+00  0.941220441D+05-0.177099343D+03

```

## Comments to Molecular Data, Heat Capacity, Entropy, and Enthalpy Increment

(2a) The structural data (Z-matrix and Cartesian coordinates) are the results obtained from G3MP2B3 *ab initio* computations carried out at  $C_s$  symmetry.<sup>7</sup> Note that the underlying B3LYP calculations, when using the 6-31G(d) basis set, optimize at a structure that is nearly  $C_s$  in symmetry, rather than truly  $C_s$  symmetry.<sup>7,34</sup> The optimized  $C_1$  ground state and the constrained  $C_s$  ground-state structures obtained at the B3LYP/6-31G(d) level differ insignificantly ( $0.02 \times 10^{-3} E_h$ , or  $4\text{ cm}^{-1}$ ) in energy.<sup>7,34</sup> With more extensive basis sets, such as 6-31+G(d,p) or 6-311G(d), the B3LYP method optimizes at the expected  $C_s$  geometry.<sup>34</sup> The transition-state structure at the top of the barrier for the  $\text{CH}_3$  internal rotation optimizes at a  $C_s$  geometry even at the B3LYP/6-31G(d) level of theory.<sup>34</sup> Note that the slight optimization problem for the ethoxyl ground-state structure using the methods de-

scribed above does not impact the thermochemical functions presented here.

(2b) The principal moments of inertia correspond to  $A_e = 1.315\text{ cm}^{-1}$ ,  $B_e = 0.318\text{ cm}^{-1}$ ,  $C_e = 0.283\text{ cm}^{-1}$ , and the rotational constant of the internal rotation is  $B_{\text{int}} = 6.505\text{ cm}^{-1}$ , which were used in the calculations of thermochemical functions. These rotational constants were extracted from the optimized  $C_1$  (nearly  $C_s$ ) B3LYP/6-31G(d) structure [see (2a) above]. The constrained  $C_s$  structure results in very similar values.

(2c) Only five vibrational frequencies are known experimentally.<sup>35,36</sup> The listed vibrational wave numbers are those obtained from the optimized  $C_1$  (nearly  $C_s$ ) B3LYP/6-31G(d) structure [see (2a) above]. The listed frequencies are scaled using the scaling factor of 0.9614.<sup>37</sup> The last listed wave number is a pseudovibration corresponding to the  $\text{CH}_3$  internal rotor. Where comparison can be made, the listed wave numbers are in reasonable agreement with the five ex-

perimental values. The listed wave numbers are also reasonably similar to those obtained from MP2(full)/6-31G(d,p) computations.<sup>32</sup>

(2d) Ethoxyl radical has a low-lying excited electronic state ( $\tilde{A}^2A'$ ) observed experimentally by Ramond *et al.*,<sup>17</sup> who determined its excitation as  $T_0 = 355 \pm 10 \text{ cm}^{-1}$ . The listed spectroscopic constants are those derived from a G3//B3LYP calculation.<sup>34</sup> At this level of theory, the excitation is  $T_0 = 340 \text{ cm}^{-1}$  ( $4.07 \text{ kJ mol}^{-1}$ ), in excellent agreement with the experimental value. The listed moments of inertia correspond to  $A_e = 1.167 \text{ cm}^{-1}$ ,  $B_e = 0.344 \text{ cm}^{-1}$ ,  $C_e = 0.296 \text{ cm}^{-1}$ , and the rotational constant of the internal rotation,  $B_{\text{int}} = 6.398 \text{ cm}^{-1}$ . The listed vibrational wave numbers are scaled by 0.9614.<sup>37</sup> The last listed wave number is a pseudovibration corresponding to the  $\text{CH}_3$  internal rotor.

(2e) The heat capacities, entropies and enthalpy increments were calculated using the rigid rotor-harmonic oscillator approach. The molecular constants of  $\text{CH}_3\text{CH}_2\text{O}$  are those listed above. The calculations include the first excited electronic state of ethoxyl ( $\tilde{A}^2A'$ ). The torsion motions in both the ground and excited states were treated as hindered rotors.

In the ground state of ethoxyl ( $\tilde{X}^2A''$ ), the barrier at the G3//B3LYP level of theory<sup>34</sup> is  $737 \text{ cm}^{-1} = 8.82 \text{ kJ mol}^{-1}$  (including zero-point-energy corrections). In the low-lying excited state ( $\tilde{A}^2A'$ ) the analogous torsion barrier is  $1030 \text{ cm}^{-1} = 12.32 \text{ kJ mol}^{-1}$ . In both states the barriers were assumed to be three-cycle sinusoidal potentials with  $\sigma_{\text{int}} = 3$ . Yamada *et al.*<sup>5</sup> have also recently performed a calculation of heat capacities, integrated heat capacities and entropies for several selected temperatures using the results of CBS-q//MP2(full)/6-31G(d,p) and G2 calculations and estimated the contribution of the internal rotor by using the tabulated values of Pitzer and Gwinn.<sup>38</sup> However, they did not include the low-lying  $\tilde{A}$  state of ethoxyl. Apart from the exclusion of the excited state, their G2-based calculations are roughly commensurate with the present results. However, the inclusion of the excited state changes the thermochemical functions rather significantly.

(2f) The standard heat capacity, entropy, and enthalpy increment values reported in the *Thermochemical Database for Combustion*<sup>13</sup> are  $C_p^\circ(298.15 \text{ K}) = 56.615 \text{ J K}^{-1} \text{ mol}^{-1}$ ,  $S^\circ(298.15 \text{ K}) = 268.589 \text{ J K}^{-1} \text{ mol}^{-1}$ , and those obtained from G3MP2B3 computations<sup>7</sup> are  $C_p^\circ(298.15 \text{ K}) = 64.44 \text{ J K}^{-1} \text{ mol}^{-1}$ ,  $S^\circ(298.15 \text{ K}) = 273.37 \text{ J K}^{-1} \text{ mol}^{-1}$ ,  $H^\circ(298.15 \text{ K}) - H^\circ(0 \text{ K}) = 12.90 \text{ kJ mol}^{-1}$ .

## References

- V. F. DeTuri and K. M. Ervin, *J. Phys. Chem. A* **103**, 6911 (1999).
- L. A. Curtiss, K. Raghavachari, P. C. Redfern, and B. S. Stefanov, *J. Chem. Phys.* **108**, 692 (1998).
- L. A. Curtiss, K. Raghavachari, P. C. Redfern, V. Rassolov, and J. A. Pople, *J. Chem. Phys.* **109**, 7764 (1998).
- F. Caralp, P. Devolder, C. Fittschen, N. Gomez, H. Hippler, R. Méreau, M. T. Rayez, F. Striebel, and B. Viskolcz, *Phys. Chem. Chem. Phys.* **1**, 2935 (1999).
- T. Yamada, J. W. Bozzelli, and T. Lay, *J. Phys. Chem.* **103**, 7646 (1999).
- S. Parthiban and J. M. L. Martin, *J. Chem. Phys.* **114**, 6014 (2001).
- R. Janoschek and M. J. Rossi, *Int. J. Chem. Kinet.* **34**, 550 (2002).
- D. F. McMillen and D. M. Golden, *Ann. Rev. Phys. Chem.* **33**, 493 (1982).
- L. Batt, *Int. Rev. Phys. Chem.* **6**, 53 (1987).
- J. Berkowitz, G. B. Ellison, and D. Gutman, *J. Phys. Chem.* **98**, 2744 (1994).
- R. Atkinson, D. L. Baulch, R. A. Cox, R. F. Hampson, Jr., J. A. Kerr, M. J. Rossi, and J. Troe, *J. Phys. Chem. Ref. Data* **29**, 167 (2000).
- J. A. Kerr and D. W. Stocker, *Strengths of Chemical Bonds*, in *CRC Handbook of Chemistry and Physics*, 81st ed. (CRC, Boca Raton, FL, 2000–2001).
- A. Burcat, TAE Report No.867, Technion, Haifa, 2001; see also <ftp://ftp.technion.ac.il/pub/supported/aetdd/thermodynamics>.
- S. P. Sander, R. R. Friedl, D. M. Golden, M. J. Kurylo, R. E. Huie, V. L. Orkin, G. K. Moortgat, A. R. Ravishankara, C. E. Kolb, M. J. Molina, and B. J. Finlayson-Pitts, JPL Publication 02-25, NASA and JPL, February 1, 2003.
- B. Ruscic, A. F. Wagner, L. B. Harding, R. L. Asher, D. Feller, D. A. Dixon, K. A. Peterson, Y. Song, X. Qian, C.-Y. Ng, J. Liu, W. Chen, and D. W. Schwenke, *J. Phys. Chem. A* **106**, 2727 (2002).
- K. M. Ervin and V. F. DeTuri, *J. Phys. Chem. A* **106**, 9947 (2002).
- T. M. Ramond, G. E. Davico, R. L. Schwartz, and W. C. Lineberger, *J. Chem. Phys.* **112**, 1158 (2000).
- G. W. Erickson, *J. Phys. Chem. Ref. Data* **6**, 831 (1977).
- L. V. Gurvich, I. V. Veyts, and C. B. Alcock, *Thermodynamic Properties of Individual Substances*, 4th ed. (Hemisphere, New York, 1991), Vol. 2.
- J. D. Cox, D. D. Wagman, and V. A. Medvedev, *CODATA Key Values for Thermodynamics* (Hemisphere, New York, 1998), (<http://www.codata.org/codata/databases/key1.html>)
- H. Y. Afeefy, J. F. Liebman, and S. E. Stein, *Neutral Thermochemical Data*, in *NIST Chemistry WebBook*, NIST Standard Reference Database Number 69, edited by P. J. Linstrom and W. G. Mallard (NIST, Gaithersburg, MD, 2003) (<http://webbook.nist.gov/>), July 2001 release.
- L. A. Curtiss, P. C. Redfern, K. Raghavachari, V. Rassolov, and J. A. Pople, *J. Chem. Phys.* **110**, 4703 (1999).
- L. A. Curtiss, K. Raghavachari, P. C. Redfern, and J. A. Pople, *J. Chem. Phys.* **106**, 1063 (1997).
- D. van Zee, M. F. Foltz, and C. B. Moore, *J. Phys. Chem.* **99**, 1664 (1993).
- M. W. Chase, Jr., C. A. Davies, J. R. Downey, Jr., D. J. Frurip, R. A. McDonald, and A. N. Syverud, *JANAF Thermochemical Tables*, 3rd ed., *J. Phys. Chem. Ref. Data* **14**, Suppl. 1 (1985).
- N. Cohen, *J. Phys. Chem. Ref. Data* **25**, 1411 (1996).
- D. R. Stull and H. Prophet, *JANAF Thermochemical Tables*, 2nd ed., NSRDS-NBS 37 (U.S. Government Printing Office, Washington D.C., 1971).
- D. R. Stull, E. F. Westrum, and G. C. Sinke, *The Chemical Thermodynamics of Organic Compounds* (Krieger, Malabar, FL, 1987).
- W. Tsang and R. F. Hampson, *J. Phys. Chem. Ref. Data* **15**, 1087 (1986).
- A. G. Baboul, L. A. Curtiss, P. C. Redfern, and K. Raghavachari, *J. Chem. Phys.* **110**, 7650 (1999).
- L. Batt, K. Christie, R. T. Milne, and A. Summers, *Int. J. Chem. Kinet.* **6**, 877 (1974).
- K. M. Ervin, S. Gronert, S. E. Barlow, M. K. Gilles, A. G. Harrison, V. M. Bierbaum, C. H. DePuy, W. C. Lineberger, and G. B. Ellison, *J. Am. Chem. Soc.* **112**, 5750 (1990).
- S. W. Benson, *Thermochemical Kinetics* (Wiley, New York, 1976).
- B. Ruscic and B. Wang (unpublished results, 2003).
- M. E. Jacox, *J. Phys. Chem. Ref. Data* **27**, 115 (1998).
- M. E. Jacox, *Vibrational and Electronic Energy Levels of Polyatomic Transient Molecules*, in *NIST Chemistry WebBook*, NIST Standard Reference Database Number 69, edited by P. J. Linstrom and W. G. Mallard (NIST, Gaithersburg, MD, 2001); (<http://webbook.nist.gov>)
- A. P. Scott and L. Radom, *J. Phys. Chem.* **100**, 16502 (1996).
- K. S. Pitzer and W. D. Gwinn, *J. Chem. Phys.* **10**, 428 (1942).

## 7.4. Miscellaneous Radicals

7.4.1. NH<sub>2</sub> Radical

## 7.4.1. Amidogen radical

13770-40-6

NH <sub>2</sub> ( <sup>2</sup> B <sub>1</sub> )	C <sub>2v</sub> (σ <sub>ext</sub> =2)
Δ <sub>f</sub> H°(298.15 K) = 186.2 ± 1.0 kJ mol <sup>-1</sup>	Δ <sub>f</sub> H°(0 K) = 189.1 ± 1.0 kJ mol <sup>-1</sup>
C <sub>p</sub> °(298.15 K) = 33.663 J K <sup>-1</sup> mol <sup>-1</sup>	H°(298.15 K) - H°(0 K) = 9.911 kJ mol <sup>-1</sup>
S°(298.15 K) = 194.868 J K <sup>-1</sup> mol <sup>-1</sup>	p° = 100 000 Pa (1 bar)

## Literature Data for the Enthalpy of Formation at 298.15 K

Δ <sub>f</sub> H°(kJ mol <sup>-1</sup> )	Authors and Reference	Method <sup>a</sup>	Comments
<b>Measurements</b>			
187.4 <sup>b</sup> ± 2.0 <sup>c</sup>	Gibson <i>et al.</i> (1985) <sup>1</sup>	PIMS-PIC	(1a)
191 ± 6 <sup>c</sup>	Hack <i>et al.</i> (1986) <sup>2</sup>	KE	(1b)
189.5 ± 3.6 <sup>c</sup>	Sutherland and Michael (1988) <sup>3</sup>	KE	(1c)
186.12 <sup>b</sup> ± 0.42 <sup>c</sup>	Mordaunt <i>et al.</i> (1996) <sup>4</sup>	DD	(1d)
<b>Computations</b>			
192 ± 10	Melius and Binkley (1988) <sup>5</sup>	BAC-MP4	(1e)
185.8 <sup>b</sup> ± 7.4 <sup>c</sup>	Mebel <i>et al.</i> (1995) <sup>6</sup>	G2M(RCC)	(1f)
183.3 ± 2.5	Espinosa-Garcia <i>et al.</i> (1995) <sup>7</sup>	QCISD(T)	(1g)
190.4 ± 13 <sup>c</sup>	Curtiss <i>et al.</i> (1998) <sup>8</sup>	CBS-Q	(1h)
186.2 ± 7.9 <sup>c</sup>	Curtiss <i>et al.</i> (1998) <sup>9</sup>	G3	(1i)
186.9 <sup>b</sup>	Mebel and Lin (1999) <sup>10</sup>	G2M(RCC)	(1j)
185.8 ± 1.9 <sup>c</sup>	Parthiban and Martin (2001) <sup>11</sup>	W2	(1k)
184.8 ± 7.8 <sup>c</sup>	Janoschek and Rossi (2002) <sup>12</sup>	G3MP2B3	(1l)
184.9	Demaison <i>et al.</i> (2003) <sup>13</sup>	CCSD(T)	(1m)
<b>Reviews and Evaluations</b>			
184.9	NBS (1982) <sup>14</sup>	TT-U	(1n)
185.4 ± 4.6	McMillen and Golden (1982) <sup>15</sup>	CDE	(1o)
190.4 ± 6.3	JANAF (1985) <sup>16</sup>	CDE	(1p)
189 ± 1	Anderson (1989) <sup>17</sup>	CDE	(1q)
190 ± 10	Gurvich <i>et al.</i> (1989) <sup>18</sup>	CDE	(1r)
188.7 ± 1.3	Berkowitz <i>et al.</i> (1994) <sup>19</sup>	CDE	(1s)
190.4 ± 6.3	NIST CCCBDB (1999) <sup>20</sup>	TT-A	(1t)
188.7 ± 1.3	Atkinson <i>et al.</i> (2000) <sup>21</sup>	TT-A	(1u)
184.9	CRC HCP (2001) <sup>22</sup>	TT-U	(1v)
188.7 ± 1.3	Kerr and Stocker (2000) <sup>23</sup>	TT-A	(1w)
189.135	Burcat (2001) <sup>24</sup>	TT-A	(1x)
189 <sup>b</sup> ± 1	Sander <i>et al.</i> (2003) <sup>25</sup>	TT-A	(1y)
190.4	NIST WebBook (2003) <sup>26</sup>	TT-A	(1z)

<sup>a</sup>PIMS-PIC: positive ion cycle based on combining photoionization measurements of the appearance energy ( $E_{\text{ap}}$ ) of a cation from a stable molecule with ionization energy ( $E_i$ ) of the radical; KE: kinetic equilibrium study; DD: photodissociation dynamics study; CDE: critical data evaluation; TT-U: unannotated tabulation of thermodynamic data; and TT-A: annotated tabulation of thermodynamic data.

<sup>b</sup>The quoted value was either not given explicitly by the author(s) or it was recalculated using auxiliary thermochemical values that differ from those used by the original authors; see individual comments for additional details.

<sup>c</sup>The uncertainty was either not given explicitly by the original author(s) or it has been modified; see individual comments for further explanations.

**Comments on the Enthalpies of Formation**

(1a) Photoionization mass spectrometric study of NH<sub>2</sub> prepared by the reaction H + N<sub>2</sub>H<sub>2</sub>. The observed ionization onset was very gradual, reflecting the unfavorable Franck–Condon factors resulting from the transition from a bent NH<sub>2</sub> radical to a significantly less bent NH<sub>2</sub><sup>+</sup> ion. Using a parameterized fit of the assumed (unresolved) rotational substructure, the authors obtained an adiabatic ionization energy of

$E_{\text{i,ad}}(\text{NH}_2) = 11.14 \pm 0.01$  eV. This value is 0.32 eV lower than the value (11.46 eV) reported in an earlier photoelectron spectroscopic study.<sup>27</sup> Combining this ionization energy with the appearance threshold of the NH<sub>2</sub><sup>+</sup> fragment from NH<sub>3</sub>,  $E_{\text{ap,0}}(\text{NH}_2^+/\text{NH}_3) = 15.768 \pm 0.004$  eV obtained by McCulloh,<sup>28</sup> the authors derived  $D_0(\text{NH}_2\text{--H}) = 446.5 \pm 1.0$  kJ mol<sup>-1</sup>, and with enthalpies of formation for NH<sub>3</sub> and H they obtain  $\Delta_f H^\circ_0(\text{NH}_2) = 191.6 \pm 1.3$  kJ mol<sup>-1</sup>,

which would correspond to  $\Delta_f H^\circ_{298}(\text{NH}_2) = 188.7 \pm 1.3 \text{ kJ mol}^{-1}$ . However, in a recent private communication quoted by Song *et al.*,<sup>29</sup> Berkowitz gives a more conservative estimate of  $E_{i,\text{ad}}(\text{NH}_2) = 11.15 \pm 0.02 \text{ eV}$ . Using the latter value, together with a slightly refined<sup>29</sup>  $E_{\text{ap},0}(\text{NH}_2^+/\text{NH}_3) = 15.765 \pm 0.001 \text{ eV}$ , leads to a moderately lower value  $D_0(\text{NH}_2\text{--H}) = 445.3 \pm 1.9 \text{ kJ mol}^{-1}$ . Using auxiliary thermochemical data from *CODATA Key Values for Thermodynamics*,<sup>30</sup>  $\Delta_f H^\circ_{298}(\text{H}) = 217.998 \pm 0.006 \text{ kJ mol}^{-1}$ ,  $[H^\circ(298.15 \text{ K}) - H^\circ(0 \text{ K})](\text{H}) = 6.197 \pm 0.001 \text{ kJ mol}^{-1}$ ,  $\Delta_f H^\circ_{298}(\text{NH}_3) = -45.94 \pm 0.35 \text{ kJ mol}^{-1}$ ,  $[H^\circ(298.15 \text{ K}) - H^\circ(0 \text{ K})](\text{NH}_3) = 10.043 \pm 0.010 \text{ kJ mol}^{-1}$ , and  $[H^\circ(298.15 \text{ K}) - H^\circ(0 \text{ K})](\text{NH}_2) = 9.911 \text{ kJ mol}^{-1}$  as adopted in the present evaluation, produces  $D_{298}(\text{NH}_2\text{--H}) = 451.3 \pm 1.9 \text{ kJ mol}^{-1}$ , and hence the enthalpy of formation  $\Delta_f H^\circ_{298}(\text{NH}_2) = 187.4 \pm 2.0 \text{ kJ mol}^{-1}$ .

(1b) Reaction  $\text{NH}_2 + \text{H}_2 \rightleftharpoons \text{NH}_3 + \text{H}$  studied in a discharge flow system in both directions in the temperature range 673–1003 K under pseudo-first-order conditions. The forward reaction was investigated by monitoring the time-dependent concentration profile  $[\text{H}](t)$  using Lyman- $\alpha$  absorption, while the reverse reaction was studied by determining the  $[\text{NH}_2](t)$  profile with LIF. The rate coefficients are represented by the Arrhenius expressions  $k_f = 3.6 \times 10^{12} \exp[-(38 \pm 3) \text{ kJ mol}^{-1}/RT] \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  and  $k_r = 8.1 \times 10^{13} \exp[-(60.9 \pm 4) \text{ kJ mol}^{-1}/RT] \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ . In the second-law determination, from the activation energies,  $D_{850}(\text{H}_2\text{N--H}) = 465 \text{ kJ mol}^{-1}$  and in the third-law derivation, from the equilibrium constant  $K = k_f/k_r$ ,  $D_{850}(\text{H}_2\text{N--H}) = 460 \text{ kJ mol}^{-1}$  was obtained at the mean temperature of 850 K. With the integrated heat capacities from the JANAF Tables,<sup>31</sup> the authors obtain  $D_{298}(\text{H}_2\text{N--H}) = 457 \text{ kJ mol}^{-1}$  and  $D_{298}(\text{H}_2\text{N--H}) = 453 \text{ kJ mol}^{-1}$ , respectively. From the mean value of these,  $D_{298}(\text{H}_2\text{N--H}) = 455 \text{ kJ mol}^{-1}$ , the authors derive  $\Delta_f H^\circ_{298}(\text{NH}_2) = 191 \text{ kJ mol}^{-1}$  (presumably using auxiliary thermochemical values from the same edition of JANAF tables<sup>31</sup>). With the auxiliary thermochemical values given in (1a) above and using data at 850 K interpolated from Gurvich *et al.*,<sup>18</sup> the mean value for the bond dissociation energy leads to the same enthalpy of formation of amidogen. The authors do not give a clear indication of the associated uncertainty. The initially assigned uncertainty of  $\pm 4 \text{ kJ mol}^{-1}$  attempted to reflect the slight disparity between the second and third law values. However, the linear analysis performed in conjunction with determining the preferred value has suggested an amplified overall uncertainty of  $\pm 6 \text{ kJ mol}^{-1}$ .

(1c) The equilibrium constant of reaction  $\text{H} + \text{NH}_3 \rightleftharpoons \text{NH}_2 + \text{H}_2$  measured over the temperature range 900–1620 K by using a flash photolysis-shock tube apparatus. Equal concentrations of H atoms and  $\text{NH}_2$  radicals are produced from the flash photolysis of  $\text{NH}_3$ . Hydrogen atom concentration is determined from transmittance measurements of Lyman- $\alpha$  radiation. Since both  $\text{NH}_3$  and  $\text{H}_2$  are maintained in large excess, the kinetics simplifies to that of a system of two opposing first-order reactions. In the experiments, the concentrations of  $\text{H}_2$  and  $\text{NH}_3$  are chosen so that no change in

the absorbance with time is observed. Under these conditions  $k_f[\text{NH}_3] = k_r[\text{H}_2]$  and the equilibrium constant,  $K = k_f/k_r$ , is equal to  $[\text{H}_2]/[\text{NH}_3]$ . Both the second-law and the third-law derivation (with entropies taken from the JANAF Tables<sup>16</sup>) are used to obtain the reaction enthalpy in the studied temperature range. Extrapolation to 298.15 and 0 K yields  $\Delta_f H^\circ_{298}(\text{NH}_2) = 189.5 \pm 1.3 \text{ kJ mol}^{-1}$ ,  $\Delta_f H^\circ_0(\text{NH}_2) = 192.5 \pm 1.3 \text{ kJ mol}^{-1}$ , and  $D_0(\text{H}_2\text{N--H}) = 447.7 \pm 1.3 \text{ kJ mol}^{-1}$ . While the initially assigned uncertainty was kept at  $\pm 1.3 \text{ kJ mol}^{-1}$ , as suggested by the authors, the linear analysis performed in conjunction with determining the preferred value has suggested an amplified overall uncertainty of  $\pm 3.6 \text{ kJ mol}^{-1}$ .

(1d) Hydrogen Rydberg atom photofragment translational spectroscopy technique used to investigate the photodissociation dynamics of  $\text{NH}_3$  following excitation to the lowest two ( $v_2 = 0$  and 1) vibrational levels of the first excited ( $\tilde{A}^1A''_2$ ) singlet electronic state. Analysis of the respective total kinetic energy release spectra (derived from the H atom time of flight spectrum), together with energy balance considerations, provides an estimate of  $D_0(\text{H}_2\text{N--H}) = 37115 \pm 20 \text{ cm}^{-1} = 443.99 \pm 0.24 \text{ kJ mol}^{-1}$ . With auxiliary thermochemical data as in (1a) above, this produces  $D_{298}(\text{NH}_2\text{--H}) = 450.06 \pm 0.23 \text{ kJ mol}^{-1}$ , and hence the enthalpy of formation  $\Delta_f H^\circ_{298}(\text{NH}_2) = 186.12 \pm 0.42 \text{ kJ mol}^{-1}$ .

(1e) BAC-MP4 *ab initio* calculations. The authors give a generic uncertainty of  $\pm 10 \text{ kJ mol}^{-1}$ , which is taken here to roughly represent a 95% confidence limit.

(1f) Modified G2 (G2M) methods have been used to obtain atomization energies for first-row compounds. The most accurate model, called G2M(RCC), gave the 0 K atomization energy of  $170.7 \text{ kcal mol}^{-1}$  ( $714.2 \text{ kJ mol}^{-1}$ ) for  $\text{NH}_2$ . Using auxiliary thermochemical data as given in (1a) above, together with  $\Delta_f H^\circ_{298}(\text{N}) = 472.68 \pm 0.40 \text{ kJ mol}^{-1}$  and  $[H^\circ(298.15 \text{ K}) - H^\circ(0 \text{ K})](\text{N}) = 6.197 \pm 0.001 \text{ kJ mol}^{-1}$  from *CODATA Key Values for Thermodynamics*,<sup>30</sup> produces an atomization energy of  $722.9 \text{ kJ mol}^{-1}$  at 298.15 K, and hence the enthalpy of formation  $\Delta_f H^\circ_{298}(\text{NH}_2) = 185.8 \text{ kJ mol}^{-1}$ . The reported<sup>6</sup> average absolute deviation for this method is  $3.7 \text{ kJ mol}^{-1}$ , and has been multiplied by a factor of 2 to bring it closer to the desired 95% confidence limit.

(1g) *Ab initio* calculations using MP4, QCISD(T), CCSD(T), and multireference methods with two extended basis sets, 6-311+G(d,p) and aug-cc-pVTZ. The reaction enthalpies for isogyric and hydrogenation reactions  $\text{NH}_2 + 2\text{H} \rightarrow \text{N} + 2\text{H}_2$  and  $\text{NH}_2 + \text{H}_2 \rightarrow \text{NH}_3 + \text{H}$ , respectively, were calculated. Geometries were optimized at the MP2/6-31G(d,p) and at the QCISD(T)/6-31G(d,p) levels. Agreement was found between the predictions based on various methods (hydrogenation reaction with full correlation) and basis sets. Recommended values of  $\Delta_f H^\circ_0(\text{NH}_2) = 185.8 \pm 2.5 \text{ kJ mol}^{-1}$  and  $\Delta_f H^\circ_{298}(\text{NH}_2) = 183.3 \pm 2.5 \text{ kJ mol}^{-1}$  were reported. It is assumed that the intent of the quoted uncertainty is to reflect a 95% confidence limit.

(1h) CBS-Q calculation. The value listed in the table is con-



verted from  $45.5 \text{ kcal mol}^{-1}$ . The reported average absolute deviation of  $1.57 \text{ kcal mol}^{-1}$  was multiplied by 2 to bring it closer to the desired 95% confidence limit. The equivalent CBS-q and CBS-4 enthalpies of formation are  $189.1 \pm 18 \text{ kJ mol}^{-1}$  ( $45.2 \text{ kcal mol}^{-1}$ ) and  $190.8 \pm 26 \text{ kJ mol}^{-1}$  ( $45.6 \text{ kcal mol}^{-1}$ ), where the uncertainties have been obtained in an analogous way.

(li) G3 *ab initio* calculation. The value listed in the table is converted from  $44.5 \text{ kcal mol}^{-1}$ . The uncertainty quoted in the table corresponds approximately to 95% confidence limits, based on twice the average absolute deviation of  $0.94 \text{ kcal mol}^{-1}$  for the enthalpies in the G2/97 test set, which roughly corresponds to 1 s.d. At the G3(MP2) level of theory<sup>32</sup>  $\Delta_f H^\circ_{298}(\text{NH}_2) = 186.2 \pm 9.9 \text{ kJ mol}^{-1}$  ( $44.5 \text{ kcal mol}^{-1}$ ), where the quoted uncertainty has been derived in a similar fashion as for the G3 value. At the G2 level of theory<sup>33</sup>  $\Delta_f H^\circ_{298}(\text{NH}_2) = 188.3 \pm 13.1 \text{ kJ mol}^{-1}$  ( $45.0 \text{ kcal mol}^{-1}$ ).

(lj) Systematic *ab initio* calculations for hydrogen-exchange reactions of  $\text{NH}_2$  with methane, ethane, and propane, using the RCC variant of the modified G2 method,<sup>6</sup> G2M(RCC) [see (lg) above]. The computed N–H bond dissociation energy is  $D_0(\text{NH}_2\text{--H}) = 106.3 \text{ kcal mol}^{-1}$  ( $444.8 \text{ kJ mol}^{-1}$ ) and the C–H bond dissociation energies and reaction enthalpies are:  $\Delta_r H_0(\text{H}_2\text{N} + \text{H--CH}_3) = -1.7 \text{ kcal mol}^{-1}$  ( $-7.1 \text{ kJ mol}^{-1}$ ),  $D_0(\text{CH}_3\text{--H}) = 104.6 \text{ kcal mol}^{-1}$  ( $437.6 \text{ kJ mol}^{-1}$ );  $\Delta_r H_0(\text{H}_2\text{N} + \text{H--CH}_2\text{CH}_3) = -5.0 \text{ kcal mol}^{-1}$  ( $-20.9 \text{ kJ mol}^{-1}$ ),  $D_0(\text{CH}_3\text{CH}_2\text{--H}) = 101.3 \text{ kcal mol}^{-1}$  ( $423.8 \text{ kJ mol}^{-1}$ );  $\Delta_r H_0[\text{H}_2\text{N} + \text{H--CH}(\text{CH}_3)_2] = -7.8 \text{ kcal mol}^{-1}$  ( $-32.6 \text{ kJ mol}^{-1}$ ),  $D_0[(\text{CH}_3)_2\text{CH--H}] = 98.5 \text{ kcal mol}^{-1}$  ( $412.1 \text{ kJ mol}^{-1}$ );  $\Delta_r H_0(\text{H}_2\text{N} + \text{H--CH}_2\text{CH}_2\text{CH}_3) = -4.6 \text{ kcal mol}^{-1}$  ( $-19.2 \text{ kJ mol}^{-1}$ ),  $D_0(\text{CH}_3\text{CH}_2\text{CH}_2\text{--H}) = 101.8 \text{ kcal mol}^{-1}$  ( $425.9 \text{ kJ mol}^{-1}$ ). From these quantities  $D_0(\text{H}_2\text{N--H}) = 444.8 \text{ kJ mol}^{-1}$  and, with auxiliary data as given in (la) above,  $D_{298}(\text{H}_2\text{N--H}) = 450.9 \text{ kJ mol}^{-1}$  can be obtained, and hence  $\Delta_f H^\circ_{298}(\text{NH}_2) = 186.9 \text{ kJ mol}^{-1}$ .

(lk) W2 *ab initio* calculation. The uncertainty quoted in the table corresponds approximately to 95% confidence limits based on twice the average absolute deviation for the W2 test set of  $0.23 \text{ kcal mol}^{-1}$ , which corresponds roughly to one standard deviation. At the W1 level of theory  $\Delta_f H^\circ_{298}(\text{NH}_2) = 185.1 \pm 3.1 \text{ kJ mol}^{-1}$ , where the uncertainty has been obtained in an analogous way.

(ll) G3(MP2)//B3LYP *ab initio* calculations for 32 selected free radicals. The uncertainty given in the table corresponds approximately to 95% confidence limits based on twice the quoted average absolute deviation of  $3.9 \text{ kJ mol}^{-1}$  for the calculated set of radicals, which corresponds roughly to 1 s.d. Note that the average absolute deviation for all enthalpies in the G2/97 test set using the same method is very slightly larger:<sup>34</sup>  $4.7 \text{ kJ mol}^{-1}$  [see also (li) above].

(lm) CCSD(T)/aug-cc-pVnZ (up to  $n=4$ ) *ab initio* calculations extrapolated to complete basis set and corrected for core–valence effects. The authors obtained the  $\text{NH}_2$  atomization energy of  $715.1 \text{ kJ mol}^{-1}$ . Using auxiliary thermochemical data listed in (la) above leads to an atomization

energy of  $723.8 \text{ kJ mol}^{-1}$  at 298.15 K, and hence the enthalpy of formation  $\Delta_f H^\circ_{298}(\text{NH}_2) = 184.9 \text{ kJ mol}^{-1}$ .

(ln) Critical data evaluation, but does not provide a pedigree of the selected value nor does it quote uncertainties.

(lo) Recommended value from extensive evaluation of data (mainly kinetic determinations) published till 1981. The reported value is primarily based on one previous kinetic determination.

(lp) Extensive compilation of thermodynamic data. The  $\text{NH}_2$  properties were last revised in June 1977. The selected value is based on kinetic determinations. The  $\text{NH}_2$  properties have not been revised in the new edition.<sup>35</sup>

(lq) A critical literature survey of the enthalpies of formation of  $\text{NH}_2$  published between 1975 and 1987. The author concludes that the result published by Gibson *et al.*<sup>1</sup> and by Sutherland and Michael<sup>3</sup> [see (1a) and (1c) above] have much higher precision than all the other measurements. Therefore,  $\Delta_f H^\circ_0(\text{NH}_2) = 192 \pm 1 \text{ kJ mol}^{-1}$  is recommended which corresponds to  $\Delta_f H^\circ_{298}(\text{NH}_2) = 189.1 \pm 1.0 \text{ kJ mol}^{-1}$ .

(lr) An extensive compilation and evaluation of thermodynamic properties. The selected value of  $\Delta_f H^\circ_{298}(\text{NH}_2) = 190 \pm 10 \text{ kJ mol}^{-1}$  is based on kinetic investigations (mainly pyrolysis studies) of reactions involving  $\text{NH}_2$ . The value is unchanged from the previous (Russian) edition.<sup>36</sup>

(ls) Critical data evaluation of R–H bond dissociation energies based on three methods: kinetic determinations, positive ion cycle determinations from photoelectron/photoionization measurements and negative ion cycle determinations from photoelectron measurements of negative ions combined with gas phase acidities. The recommended value is that originally reported by Gibson *et al.*<sup>1</sup> [see (1a) above].

(lt) The compilation lists theoretical results at various levels of theory, but also makes a reference to one experimental benchmark. The quoted experimental benchmark value is from the JANAF Tables<sup>16,35</sup> [see (1p) above].

(lu) Critical evaluation of atmospherically relevant kinetic rates. Their table of enthalpy data lists Kerr and Stocker<sup>23</sup> [see (1w) below] as their source of  $\Delta_f H^\circ_{298}(\text{NH}_2)$ , who in turn adopt the recommendation of Berkowitz *et al.*<sup>19</sup> [see (1s) above].

(lv) The tabulation gives a list of compilations as sources, but no specific references for individual species. However, the value appears to correspond to that adopted by NBS Tables<sup>14</sup> [see (1n) above].

(lw) Thermodynamic data compilation. The listed value is that reported by Berkowitz *et al.*<sup>19</sup> [see (1s) above].

(lx) Thermodynamic database for combustion. Burcat quotes Anderson<sup>17</sup> [see (1q) above] as the source of  $\Delta_f H^\circ_{298}(\text{NH}_2)$ .

(ly) Critical evaluation of atmospherically relevant kinetic data. The quoted value,  $186 \pm 1 \text{ kJ mol}^{-1}$ , must be a typographical error, because they quote Anderson<sup>17</sup> [see (1q) above] as the source of  $\Delta_f H^\circ_{298}(\text{NH}_2)$ .

(lz) An unevaluated tabulation of available values from other sources. The source for the listed value are the JANAF Tables<sup>16,35</sup> [see (1p) above].

## Preferred Value of the Enthalpy of Formation

$$\Delta_f H^\circ(298.15 \text{ K}) = 186.2 \pm 1.0 \text{ kJ mol}^{-1}$$

$$\Delta_f H^\circ(0 \text{ K}) = 189.1 \pm 1.0 \text{ kJ mol}^{-1}$$

The four experimental measurements published since the review of McMillen and Golden<sup>15</sup> are in reasonable agreement, although the photofragment measurement of Mordaunt *et al.*,<sup>4</sup> which claims the highest accuracy, produces the lowest value. The two kinetic measurements, by Hack *et al.*<sup>2</sup> and by Sutherland and Michael,<sup>3</sup> seem to imply a value only slightly higher than the original photoionization result of Gibson *et al.*,<sup>1</sup> which was subsequently recommended in several compilations. However, after the recent conservative revision of the ionization energy of Gibson *et al.*<sup>1</sup> [see (1a) above], which lowers the resulting enthalpy by 1.3 kJ mol<sup>-1</sup>, the photoionization result falls somewhat closer to the photofragment “low” value than to the two “high” kinetic values. At the same time, newer calculations lend further credence to the value obtained by Mordaunt *et al.*<sup>4</sup> It should be also noted that the two older tabulations (NBS<sup>14</sup> and McMillen and Golden<sup>15</sup>) seem to imply a lower value.

With the originally assigned uncertainties, the weighted average of all four measurements produces a 298.15 K enthalpy of formation of amidogen of 186.5 ± 2.0 kJ mol<sup>-1</sup>. However, further linear analysis shows that the uncertainties of the two kinetic measurements<sup>2,3</sup> would have to be amplified to ±6 and 3.6 kJ mol<sup>-1</sup>, respectively, in order to achieve full harmony within the set. With these amplified

uncertainties the weighted average shifts slightly to 186.2 ± 1.0 kJ mol<sup>-1</sup>, which is the currently preferred value. The preferred value is in excellent accord with the value of Mordaunt *et al.*<sup>4</sup> At the same time, the weighted average of the photoionization result and the two kinetic results (excluding the photofragment result), which is 189.0 ± 3.3 kJ mol<sup>-1</sup>, is in accord with the preferred value, largely because of the higher associated uncertainty. Finally, the weighted average of the listed calculations (where, for the purpose of averaging, the calculation of Mebel and Lin<sup>10</sup> has been assigned an uncertainty of ±7 kJ mol<sup>-1</sup>, and the calculation of Demaison<sup>13</sup> has been assigned an estimated uncertainty of ±2 kJ mol<sup>-1</sup>), is 185.1 ± 1.1 kJ mol<sup>-1</sup>, in reasonable accord with the preferred value.

The preferred value corresponds to the N–H bond dissociation energy in ammonia  $D_{298}(\text{H}_2\text{N}-\text{H}) = 450.2 \pm 1.1 \text{ kJ mol}^{-1}$  (444.1 ± 1.1 kJ mol<sup>-1</sup> at 0 K), which produces the listed enthalpy when used together with auxiliary thermochemical values from CODATA:<sup>30</sup>  $\Delta_f H^\circ_{298}(\text{H}) = 217.998 \pm 0.006 \text{ kJ mol}^{-1}$ ,  $[H^\circ(298.15 \text{ K}) - H^\circ(0 \text{ K})] \times (\text{H}) = 6.197 \pm 0.001 \text{ kJ mol}^{-1}$ ,  $\Delta_f H^\circ_{298}(\text{NH}_3) = -45.94 \pm 0.35 \text{ kJ mol}^{-1}$ ,  $[H^\circ(298.15 \text{ K}) - H^\circ(0 \text{ K})](\text{NH}_3) = 10.043 \pm 0.010 \text{ kJ mol}^{-1}$ ,  $[H^\circ(298.15 \text{ K}) - H^\circ(0 \text{ K})](\text{H}_2) = 8.468 \pm 0.001 \text{ kJ mol}^{-1}$  and  $[H^\circ(298.15 \text{ K}) - H^\circ(0 \text{ K})] \times (\text{N}_2) = 8.670 \pm 0.001 \text{ kJ mol}^{-1}$ , together with  $[H^\circ(298.15 \text{ K}) - H^\circ(0 \text{ K})](\text{NH}_2) = 9.929 \text{ kJ mol}^{-1}$  as listed below.

Geometry (distance in Å, angles in degrees)<sup>(2a)</sup>

Z matrix				Cartesian coordinates				
				x	y	z		
N			N	0.000 000	0.080 388	0.000 000		
H	1	1.0263	H	0.000 000	-0.558 470	-0.803 226		
H	2	1.0263	2	103.005	H	0.000 000	-0.558 470	0.803 226
Moments of inertia in the electronic ground state <sup>(2b)</sup>								
$I = 1.181 \times 10^{-47} \text{ kg m}^2$			$I_B = 2.161 \times 10^{-47} \text{ kg m}^2$		$I_C = 3.425 \times 10^{-47} \text{ kg m}^2$			
Vibrational wave numbers in the electronic ground state $\nu_i(\text{cm}^{-1})$ <sup>(2c)</sup>								
3119.37 ( $a_1$ )			1497.32 ( $a_1$ )		3301.11 ( $b_2$ )			

Excited Electronic States<sup>(2d)</sup>

$$\text{Term value: } T_0[\tilde{A}^2 A_1(\Pi_u)] = 11\,122.6 \text{ cm}^{-1} (C_{2v}, \sigma_{\text{ext}} = 2)$$

Heat Capacity  $C_p^\circ$ , Entropy  $S^\circ$ , and Enthalpy Increment  $[H^\circ(T) - H^\circ(0\text{ K})]^{(2e),(2f)}$ 

$T/\text{K}$	$C_p^\circ(T)$ ( $\text{J K}^{-1} \text{mol}^{-1}$ )	$S^\circ(T)$ ( $\text{J K}^{-1} \text{mol}^{-1}$ )	$[H^\circ(T) - H^\circ(0\text{ K})]$ ( $\text{kJ mol}^{-1}$ )
100	33.303	158.413	3.294
200	33.350	181.508	6.626
298.15	33.663	194.868	9.911
300	33.674	195.076	9.973
400	34.477	204.863	13.377
500	35.594	212.672	16.879
600	36.879	219.274	20.502
800	39.728	230.268	28.157
1000	42.650	239.448	36.397
1200	45.344	247.467	45.203
1500	48.693	257.962	59.329
2000	52.605	272.549	84.729
2500	55.152	284.582	111.716
3000	56.874	294.806	139.768

## 7-Constant NASA Polynomial

```

AMIDOGEN RADICAL JUN03 N 1.H 2. 0. 0.G 200.000 3000.000 16.02258 1
0.25926305E+01 0.34768360E-02-0.10827162E-05 0.14934256E-09-0.57524119E-14 2
0.21573834E+05 0.79056535E+01 0.41919802E+01-0.20460283E-02 0.66775613E-05 3
-0.52490724E-08 0.15558995E-11 0.21186431E+05-0.90478524E-01 0.22394687E+05 4

```

## 9-Constant NASA Polynomial

```

AMIDOGEN RADICAL IUPAC Task Group on Selected Radicals
2 JUN03 N 1.00H 2.00 0.00 0.00 0.00 0 16.02258 186200.000
200.000 1000.0007 -2.0 -1.0 0.0 1.0 2.0 3.0 4.0 0.0 9911.000
-0.279034459D+05 0.425771986D+03 0.165260988D+01 0.552646387D-02-0.522162435D-05
0.411234091D-08-0.133807400D-11 0.000000000D+00 0.191754999D+05 0.138430812D+02
1000.000 3000.0007 -2.0 -1.0 0.0 1.0 2.0 3.0 4.0 0.0 9911.000
-0.105603368D+07 0.601536996D+04-0.956589200D+01 0.152474093D-01-0.698658949D-05
0.162676281D-08-0.151442119D-12 0.000000000D+00-0.131337863D+05 0.881066848D+02

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## Comments on Molecular Data, Heat Capacity, Entropy, and Enthalpy Increment

(2a) The structural data ( $Z$  matrix and Cartesian coordinates) are based on the QCISD(T)/[ $5s4p2d2f,3s2p$ ] force field computation of Martin *et al.*<sup>37</sup> [see also (2b) and (2e) below], where the equilibrium N–H bond length of 1.026 31 Å and H–N–H angle of 103.005° were obtained.

(2b) The listed moments of inertia correspond to experimental rotational constants<sup>38</sup>  $A_0 = 23.693 \text{ cm}^{-1}$ ,  $B_0 = 12.952 \text{ cm}^{-1}$ , and  $C_0 = 8.173 \text{ cm}^{-1}$ . The equivalent values computed<sup>37</sup> at the QCISD(T)/[ $5s4p2d2f,3s2p$ ] level are 23.600, 12.848, and 8.138  $\text{cm}^{-1}$ , respectively [see also (2e) below].

(2c) The listed vibrational wave numbers are experimentally determined fundamentals.<sup>38</sup> The equivalent values computed<sup>37</sup> at the QCISD(T)/[ $5s4p2d2f,3s2p$ ] level are 3218.9, 1502.1, and 3298.5  $\text{cm}^{-1}$ , respectively [see also (2e) below].

(2d) The listed term value of the  $\tilde{A}^2A_1(\Pi_u)$  excited state has been experimentally determined.<sup>38</sup> The state is pseudolinear with a barrier to linearity of 730  $\text{cm}^{-1}$ .<sup>38</sup>

(2e) The heat capacities, enthalpy increments, and entropies were adopted from Martin *et al.*<sup>37</sup> These authors have com-

puted an anharmonic potential surface of  $\text{NH}_2$  at the all-electron QCISD(T)/[ $5s4p2d2f,3s2p$ ] level and obtained detailed spectroscopic constants that are—to the extent comparison is possible—not only in excellent agreement with experiment, but provide much more detail with respect to anharmonic terms, rovibrational coupling, and centrifugal distortion. Using a hybrid analytic/direct summation method, Martin *et al.*<sup>37</sup> have computed the thermodynamic functions including exact accounts for anharmonicity and rovibrational coupling, and very good analytical approximations to centrifugal distortion and quantum rotation effects. The  $\tilde{A}^2A_1(\Pi_u)$  excited state of amidogen (located<sup>37,38</sup> at about 11 000  $\text{cm}^{-1}$ ) was also taken into account, albeit using a rigid rotor-harmonic oscillator approach. Martin *et al.*<sup>37</sup> note that the effect of the inclusion of the excited state becomes significant around 2000 K, and that in order to obtain more accurate thermodynamic functions beyond 3000 K, the excited state contribution would need to include experimentally unknown (and computationally very challenging) anharmonic effects and rovibrational coupling in an approach similar to that taken for the ground state of amidogen.

(2f) The standard heat capacity, entropy, and enthalpy increment values reported in the NBS Tables<sup>14</sup> are

$C_p^\circ(298.15\text{ K}) = 33.85\text{ J K}^{-1}\text{ mol}^{-1}$ ,  $S^\circ(298.15\text{ K}) = 195.00\text{ J K}^{-1}\text{ mol}^{-1}$ ,  $[H^\circ(298.15\text{ K}) - H^\circ(0\text{ K})](\text{NH}_2) = 9.937\text{ kJ mol}^{-1}$ , in the JANAF<sup>16</sup> and NIST-JANAF<sup>35</sup> Thermochemical Tables are  $C_p^\circ(298.15\text{ K}) = 33.572\text{ J K}^{-1}\text{ mol}^{-1}$ ,  $S^\circ(298.15\text{ K}) = 194.707\text{ J K}^{-1}\text{ mol}^{-1}$ ,  $[H^\circ(298.15\text{ K}) - H^\circ(0\text{ K})](\text{NH}_2) = 9.929\text{ kJ mol}^{-1}$ , in the compilation by Gurvich *et al.*<sup>18</sup> are  $C_p^\circ(298.15\text{ K}) = 33.857\text{ J K}^{-1}\text{ mol}^{-1}$ ,  $S^\circ(298.15\text{ K}) = 194.991\text{ J K}^{-1}\text{ mol}^{-1}$ ,  $[H^\circ(298.15\text{ K}) - H^\circ(0\text{ K})](\text{NH}_2) = 9.938\text{ kJ mol}^{-1}$ , in the *Thermochemical Database for Combustion*<sup>24</sup> are  $C_p^\circ(298.15\text{ K}) = 33.857\text{ J K}^{-1}\text{ mol}^{-1}$ ,  $S^\circ(298.15\text{ K}) = 194.996\text{ J K}^{-1}\text{ mol}^{-1}$ , and those obtained from G3MP2B3 computations<sup>12</sup> are  $C_p^\circ(298.15\text{ K}) = 33.59\text{ J K}^{-1}\text{ mol}^{-1}$ ,  $S^\circ(298.15\text{ K}) = 194.77\text{ J K}^{-1}\text{ mol}^{-1}$ ,  $[H^\circ(298.15\text{ K}) - H^\circ(0\text{ K})](\text{NH}_2) = 9.93\text{ kJ mol}^{-1}$ .

## References

- S. T. Gibson, J. P. Greene, and J. Berkowitz, *J. Chem. Phys.* **83**, 4319 (1985).
- W. Hack, P. Rouveiolles, and H. Gg. Wagner, *J. Phys. Chem.* **90**, 2505 (1986).
- J. W. Sutherland and J. V. Michael, *J. Chem. Phys.* **88**, 830 (1988).
- D. H. Mordant, M. N. R. Ashfold, and R. N. Dixon, *J. Chem. Phys.* **104**, 6460 (1996).
- C. F. Melius and J. S. Binkley, Proceedings 21st Symposium (Int.) Combustion **21**, 1953 (The Combustion Institute, Pittsburgh, PA, 1986), Vol. 21; see also <http://z.ca.sandia.gov/~mmelius/>
- A. M. Mebel, K. Morokuma, and M. C. Lin, *J. Chem. Phys.* **103**, 7414 (1995).
- J. Espinosa-Garcia, J. C. Corchado, J. Fernández, and A. Marquez, *Chem. Phys. Lett.* **233**, 220 (1995).
- L. A. Curtiss, K. Raghavachari, P. C. Redfern, and B. S. Stefanov, *J. Chem. Phys.* **108**, 692 (1998).
- L. A. Curtiss, K. Raghavachari, P. C. Redfern, V. Rassolov, and J. A. Pople, *J. Chem. Phys.* **109**, 7764 (1998).
- A. M. Mebel and M. C. Lin, *J. Phys. Chem. A* **103**, 2088 (1999).
- S. Parthiban and J. M. L. Martin, *J. Chem. Phys.* **114**, 6014 (2001).
- R. Janoschek and M. J. Rossi, *Int. J. Chem. Kinet.* **34**, 550 (2002).
- J. Demaison, L. Margulès, and J. E. Boggs, *Phys. Chem. Chem. Phys.* **5**, 3359 (2003).
- D. D. Wagman, W. E. Evans, V. B. Parker, R. H. Schumm, I. Halow, S. M. Bailey, K. L. Churney, and R. L. Nuttall, The NBS Tables of Chemical Thermodynamic Properties, *J. Phys. Chem. Ref. Data* **11**, Suppl. 2 (1982).
- D. F. McMillen and D. M. Golden, *Annu. Rev. Phys. Chem.* **33**, 493 (1982).
- M. W. Chase, Jr., C. A. Davies, J. R. Downey, Jr., D. J. Frurip, R. A. McDonald, and A. N. Syverud, JANAF Thermochemical Tables, 3rd ed., *J. Phys. Chem. Ref. Data* **14**, Suppl. 1 (1985).
- W. R. Anderson, *J. Phys. Chem.* **93**, 530 (1989).
- L. V. Gurvich, I. V. Veits, and C. B. Alcock, *Thermodynamic Properties of Individual Substances*, 4th ed. (Hemisphere, New York, 1989), Vol. 1.
- J. Berkowitz, G. B. Ellison, and D. Gutman, *J. Phys. Chem.* **98**, 2744 (1994).
- Computational Chemistry Comparison and Benchmark DataBase (CCCBDB), NIST 1999; see <http://srdata.nist.gov/cccbdb/>
- R. Atkinson, D. L. Baulch, R. A. Cox, R. F. Hampson, Jr., J. A. Kerr, M. J. Rossi, and J. Troe, *J. Phys. Chem. Ref. Data* **29**, 167 (2000).
- Standard Thermodynamic Properties of Chemical Substances*, in *CRC Handbook of Chemistry and Physics*, edited by D. Lide, 82nd ed. (CRC, Boca Raton, FL, 2001–2002).
- J. A. Kerr and D. W. Stocker, *Strengths of Chemical Bonds*, in *CRC Handbook of Chemistry and Physics*, edited by D. Lide, 82nd ed. (CRC, Boca Raton, FL, 2001–2002).
- A. Burcat, TAE Report No. 867, Technion, Haifa, 2001; see also <ftp://ftp.technion.ac.il/pub/supported/aetdd/thermodynamics>
- S. P. Sander, R. R. Friedl, D. M. Golden, M. J. Kurylo, R. E. Huie, V. L. Orkin, G. K. Moortgat, A. R. Ravishankara, C. E. Kolb, M. J. Molina, and B. J. Finlayson-Pitts, JPL Publication 02-25, NASA and JPL, February 1, 2003.
- H. Y. Afeefy, J. F. Liebman, and S. E. Stein, *Neutral Thermochemical Data*, in *NIST Chemistry WebBook*, NIST Standard Reference Database Number 69, edited by P. J. Linstrom and W. G. Mallard (NIST, Gaithersburg, MD, 2003); <http://webbook.nist.gov/>
- S. J. Dunlavey, J. M. Dyke, N. Jonathan, and A. Morris, *Mol. Phys.* **39**, 1121 (1980).
- K. E. McCulloh, *Int. J. Mass. Spectrom.* **21**, 333 (1976).
- Y. Song, X.-M. Qian, K.-C. Lau, and C.-Y. Ng, *J. Chem. Phys.* **115**, 2582 (2001).
- J. D. Cox, D. D. Wagman, and V. A. Medvedev, *CODATA Key Values for Thermodynamics* (Hemisphere, New York, 1989); see also <http://www.codata.org/codata/databases/key1.html>
- D. R. Stull and H. Prophet, *JANAF Thermochemical Tables*, 2nd ed., NSRDS-NBS 37 (US Gov. Printing Office, Washington, DC, 1971).
- L. A. Curtiss, P. C. Redfern, K. Raghavachari, V. Rassolov, and J. A. Pople, *J. Chem. Phys.* **110**, 4703 (1999).
- L. A. Curtiss, K. Raghavachari, P. C. Redfern, and J. A. Pople, *J. Chem. Phys.* **106**, 1063 (1997); see also L. A. Curtiss, L. D. Kock, and J. A. Pople, *ibid.* **95**, 4040 (1991).
- A. G. Baboul, L. A. Curtiss, P. C. Redfern, and K. Raghavachari, *J. Chem. Phys.* **110**, 7650 (1999).
- M. W. Chase, Jr., NIST-JANAF Thermochemical Tables, 4th Ed., *J. Phys. Chem. Ref. Data Monogr.* **9** (1998).
- V. P. Glushko, L. V. Gurvich, G. A. Bergman, I. V. Veits, V. A. Medvedev, G. A. Khackhuruzov, and V. S. Yungman, *Termodinamicheski Svoistva Individual'nikh Veschestv*, 3rd ed. (Nauka, Moscow, 1979).
- J. M. L. Martin, J. P. François, and R. Gijbels, *J. Chem. Phys.* **97**, 3530 (1992).
- M. E. Jacox, *J. Phys. Chem. Ref. Data* **27**, 115 (1998).