NBSIR 82-2401

Heating Values of Natural Gas and Its Components

U.S. DEPARTMENT OF COMMERCE
National Bureau of Standards
Center for Chemical Physics
Chemical Thermodynamics Division
Washington, DC 20234

May 1982

Technical Report

Issued August 1982

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George T. Armstrong
Thomas L. Jobe, Jr.

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NATIONAL BUREAU OF STANDARDS, Ernest Ambler, *Director*

Preface

The Office of Standard Reference Data of the National Bureau of Standards is responsible for a broad-based program to provide reliable physical and chemical reference data to the U.S. technical community. Under this program a number of data evaluation centers both at NBS and at universities and other private institutions are supported and coordinated; these activities are collectively known as the National Standard Reference Data System (NSRDS). Important areas of the physical sciences are covered systematically by NSRDS data centers, and data bases with broad utility are prepared and disseminated. These centers can also take on special compilations of data addressing specific applications. The existence of an ongoing program permits the collection of data for these special compilations to be carried out in an efficient and timely manner.

This Report on the Heating Values of Natural Gas and Its Components was prepared with the assistance of the Chemical Thermodynamics Data Center of the National Bureau of Standards. We hope that it will provide a useful source of reference data and computational methods for all those concerned with the heating value of natural gas.

David R. Lide, Jr. Chief

Office of Standard Reference Data

Dr. George Thompson Armstrong, the senior author, died on March 9, 1982. At that time an almost complete, well written draft was at hand and had been reviewed by several of his colleagues, including myself. It has been my privilege to help prepare the final version. The original organization and wording have been retained wherever possible. Several sections have been completed, based on indications in the text. New atomic masses and heat capacities have been selected and a discussion of the enthalpy of combustion of methane (in Appendix 7) has been written. All of these were influenced by notes and letters, but, at times, go beyond them. I hope that the spirit and quality of the original has been maintained.

There is one section missing: acknowledgements. Neither Mr. Jobe nor I can reconstruct a record of the many persons who were consulted, who advised or who sent in material. We thank all who have helped and hope that this report will both be useful to them and meet with their approval.

David Garvin

Chemical Thermodynamics Data Center

Abstract

This document gives the basic data needed, recommended procedures and illustrative calculations for computing heating values of natural gas mixtures from the composition of the mixtures and the properties of the components at commonly used reference conditions for gas measurement. Much of the data is given in the form of tables, and sufficient information is given for calculating properties at conditions other than those for which tables are given. Symbols and terms used are defined, units of measurement are defined and conversion factors and physical constants are given.

The standard enthalpies of combustion and heat capacities of the pure hydrocarbon gases C_1 to C_6 are selected from prior initial evaluations of experimental measurements. The enthalpies of combustion of the ideal gases at the reference temperatures 273.15 K (0 °C), 288.15 K (15 °C), 288.71 K (60 °F), and 298.15 K (25 °C) on a molar basis, and a volumetric basis are given. Tables are for the dry gases, and information is given to calculate the enthalpy of combustion of the ideal water-saturated gas on a volumetric basis. The calculation of enthalpies of combustion of ideal gas mixtures on a molar, mass, or volumetric basis is described.

Second virial coefficients as functions of temperature for the pure substances and for binary interactions with methane as one component are presented as selected from recent compilations based on experimental measurements.

Tables are given for molar volumes, ethalpic effects (H-H°), and the heating values of the dry real-gas hydrocarbons on a molar basis, a mass basis, and a volumetric basis at two reference conditions, 288.15 K

(15 °C), 101 325 Pa; and 288.71 (60 °F), 101 560 Pa (14.73 psia). The procedure used in calculating these tables is described and information is provided for making similar calculations for other reference conditions. An analysis of the uncertainties of the data is presented, together with procedures for calculating the propagation of errors and the effects of these errors on calculated heating values. Supporting data, sources of the data, and discussions of the relationships involved are presented in a series of appendixes.

KEYWORDS: Calorific value, enthalpy of combustion; fuel gas mixtures; heat capacities; heating value; hydrocarbons; liquefied natural gas; natural gas; propagation of errors; reference conditions.

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HEATING VALUES OF NATURAL GAS AND ITS COMPONENTS

1. Introduction

This document provides the basic information for calculating heating values of natural gas mixtures from a knowledge of the gas composition. While it was prepared specifically to meet the needs of the liquefied natural gas industry, the information is equally well applicable to native or processed natural gas mixtures that have not been liquefied.

The substances treated are the saturated hydrocarbons C_1 to C_6, a few of the more commonly encountered cyclic and unsaturated hydrocarbons, and some non-hydrocarbon gases frequently found in natural gas. A broader range of materials, but for fewer reference conditions, is given in an earlier study [1].[a]

The approximate limits of composition and other properties of gaseous fuel mixtures to which this document should apply are given in Appendix 1.

The presentation is in handbook style, with sufficient detail to allow the use of the information in a variety of ways to meet various requirements. The information is sufficient to allow calculations at various base conditions of measurement in use in the natural gas industry, to allow calculations of greater or lesser accuracy, and to allow the uncertainty of the results to be estimated.

The data and procedures given should not be construed as providing a definitive substitute for laboratory measurement of heating value, which can be reliably performed using well known standard methods of test.

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[a]Numbers in brackets in the text refer to references in the general list at the end of this document. Appendices have their own reference lists.

In many cases, however, an estimate of the calorific value is adequate. These include engineering design calculations for power plants and power plant components, in establishing the adequacy of fuels from certain sources or processes for selected purposes and in estimating processing requirements or mixing proportions needed to obtain gas mixtures of specified performance. Moreover, the estimates are pertinent and usable in custody transfer operations to the extent agreeable to the parties involved. Indeed, the study made here of the uncertainties in the estimates suggests that the calculation of heating values may be used in many routine conditions.

The organization of this document is described here with the aid of two figures. First there are necessary preliminaries: definition of reference conditions (Table 2), molecular weights and conversion factors for energy units (Table 1). Then the basic thermodynamic data are given. The starting point is a set of carefully evaluated enthalpies of formation for the ideal gases at 298.15 K (25 °C) from which best values for the enthalpies of combustion of selected hydrocarbons are derived and listed in Table 4. Properties of products of combustion and auxiliary substances are listed in Table 3. Three reference temperatures of interest here are different from that at which the basic data are reported. The enthalpies of formation and combustion are corrected from 298.15 K to these temperatures using the scheme outlined in Figure 1 and Appendix 8 and enthalpy differences from Tables 3 and 4.

The rest of the calculations are summarized in Figure 2. Starting with the molar enthalpy of combustion of the fuel as an ideal gas, point B, values are derived for the enthalpy of combustion per unit mass, point E, and per unit volume, dry and water saturated, at points C and D. These are given, for the ideal gas, in Tables 6 and 7 while the needed molar volumes are in Table 5. The procedures are in Section 9.

Real gas properties are produced by correcting the ideal gas molar enthalpy of combustion using equation of state data (second virial coefficients) in Table 8 and procedures described in section 10. This produces the real gas enthalpy of combustion, point F in Figure 2. From there the volumetric and mass based quantities are derived, points G, H and I. The real gas enthalpies of combustion at 15 °C and 60 °F are given in Tables 9 and 10, while the molar volumes and enthalpy correction factors are in Tables 11 and 12. In other tables there is enough information given to permit calculations for other conditions of temperature and pressure.

Procedures for the calculation of the properties of mixtures are developed in section 12. Both ideal and real gas mixtures are treated, with the latter being considered two ways: as a mixture of non-interacting real gases and as a mixture of interacting real gases. All treatments are based on the virial equation of state.

Uncertainties in the data are discussed in section 13. Those for the enthalpies of combustion are summarized in Table 15. These are the limiting factors on the accuracy of the data. They should be used in all calculations. The numbers in Table 15 indicate that the uncertainty in the enthalpies of combustion of interest here are of the order of tenths of kilojoules per mole, and, at times, of the order of kilojoules per mole. This means that in most tables of thermodynamic properties given here, the right-most digit is not significant. It is provided for rounding numbers in calculations made by the reader. Differences that are only in the final digit between the numbers here and in other compilations should be ignored. They are the result of slight variations in calculation and rounding procedures. Larger differences usually are due to differing choices for basic data.

2. Symbols

The symbols used in this work are listed in Appendix 2 in Table A2. They are, so far as practicable, in conformity with the recommendations of the International Union of Pure and Applied Chemistry (IUPAC) [2,3] and of the International Organization for Standardization (ISO) [4].

3. Definitions of terms

The following terms used in this document are defined in Appendix 3.

Quantitites and concepts.

- atomic weight
- compression factor
- dry gas
- enthalpy
- enthalpy of combustion
- enthalpy of formation
- equation of state
- gas constant
- heat capacity
- ideal gas
- International Practical Temperature Scale
- molar mass
- molecular weight
- net calorific value (net or lower heating value)
- real gas
- relative atomic mass
- relative molecular mass
- reference (standard) conditions
- specific heat capacity
- standard state
- total calorific value (total or gross heating value)
- vapor pressure
- virial coefficient
- volume under standard conditions
- water saturated gas

Units of measurement.

- atmosphere
- British thermal unit
- joule
- newton
- pascal
- standard cubic foot (of gas)
- torr

The usage of terms is intended to represent best current practice and to conform so far as possible to recommendations of IUPAC [2,3], ISO [4,5], and the International Bureau of Weights and Measures (BIPM) [5].

4. Units of measurement

The quantities given in this report are based on values measured or expressed in the International System of Units (SI) [5]. The conversion factors used in this document for units of energy are:

$$1055.056\ \mathrm{J} = 1\ \mathrm{Btu}_{IT}$$

$$1\ \mathrm{MJ\ m^{-3}} = 26.839\ 192\ \mathrm{Btu}_{IT}\ \mathrm{ft}^{-3}$$

(under identical conditions of temperature and pressure). See Appendix 3, section A3.2.2 for a discussion of the various Btu's. Other conversion factors are found in Table A4 (Appendix 4).

5. Physical constants

Relative atomic and molecular masses. (Atomic and molecular weights). Molecular masses used in this document are listed in Table 1a. These molecular masses are based on the 1981 recommendations of the International Union of Pure and Applied Chemistry Commission on Atomic Weights and Isotopic Abundancies [6]. Some other sets of relative atomic masses are discussed in Appendix 5a.

Other physical constants. Table 1b lists other physical constants used in this document. The value for the gas constant is that recommended by the CODATA Task Group on Fundamental Constants [7]. The acceleration of gravity and the density of mercury are part of the (historical) measurement chain for pressure, which is discussed in Appendix 5b.

Table 1. Physical constants

1a. Relative atomic and molecular masses used in this document

Substance	Relative Molecular Mass*	Substance	Relative Molecular Mass*	Substance	Relative Molecular Mass*
nonhydrocarbon		nonhydrocarbon		hydrocarbon	
Ar	39.948	O	15.9994	C_2H_6	30.070
C	12.011	O_2	31.9988	C_3H_6	42.081
CO	28.0104	S	32.06	C_3H_8	44.097
CO_2	44.0098	SO_2	64.059	C_4H_8	56.108
		hydrocarbon			
H	1.00794	CH_2	14.027	C_4H_{10}	58.123
H_2	2.0159	CH_4	16.043	C_5H_{10}	70.134
H_2O	18.0153	C_2H_2	26.038	C_5H_{12}	72.150
H_2S	34.076	C_2H_4	28.054	C_6H_6	78.114
He	4.0026			C_6H_{12}	84.161
N_2	28.0134			C_6H_{14}	86.177

*Taken from A category in Table A5a. Many molecular masses have been rounded to three decimal places after addition. Uncertainties in atomic masses are in the rightmost digit.

Table 1b. Other physical constants used in this document[a]

gas constant (R)	8.31441(26) J mol^{-1} K^{-1}
standard acceleration of gravity (g)	980.665(0) cm s^{-2}
standard density of mercury at T = 273.15 K	13.5951(0) g cm^{-3}

[a]Numbers in parentheses indicate the uncertainties in the last figures of the number listed. Zero indicates that the number is defined.

6. Reference conditions of measurement

Reference conditions of measurement for which this document is specially intended are listed in Table 2. Reference conditions, sometimes referred to as "base conditions" are in a state of flux in the gas industry. Each of the parameters (temperature, pressure, state of gas, and water content) listed in Table 2 is discussed in Appendix 6. Not all combinations of temperature, pressure, gas ideality, and water content discussed there are of probable use in the gas industry. An attempt has been made to sort out the potentially useful conditions and five conceivably useful sets of reference conditions are listed in Table 2. This document provides information necessary to convert values of properties from one to the other. However, the set labelled "ISO/ASTM/ANSI (metric units)" is considered to be the most useful for the purpose of this document, and combustion data are provided for these conditions, with the exception that real gas properties are not specifically listed for all the substances that are minor components of natural gas. Data are also given at the slightly different conditions customary in the USA, the set is labeled "ANSI/ASTM/API (U.S. Customary units)".

Table 2. Reference conditions of measurement used in this document

Designation	T^a	p^a	State of Gas	Water Content
IUPAC(new)[3]	298.15 K	100 kPa	ideal	dry
STP	273.15 K (0 °C)	101.325 kPa (760 mmHg)	real	dry
IUPAC(old)[8]	298.15 K (25 °C)	101.325 kPa (760 mmHg)	ideal	dry
ISO/ASTM/ANSI[9][a] (metric units)	288.15 K (15 °C)	101.325 kPa	real	dry/sat
ASTM/ANSI/API[9,10] (U.S. customary)	288.71 K (60 °F)	101.560 kPa (14.73 psia)	real	sat

[a]Alternative units for specifying the same temperature should not be taken to mean a different temperature. That is, 25 °C is identical to 298.15 K; 15 °C is identical to 288.15 K, and 60 °F is identical to 15.555 °C or 288.7055 ... K, in which the fraction is continuing. This is rounded to 288.71 K. Similarly, different units for expressing the same pressure should not be construed as different pressures. 101.325 kPa is identical to 760 Torr and to 760 mmHg. The value 101.560 kPa is a rounded value corresponding to 14.73 psia. This last value is taken here as exact, although it may have originated as a rounded value for 30 in Hg. (In contrast we use 288.706 K for 60 °F, not 288.71 K as appears in most table headings). See Appendix 6 for discussion of reference conditions and Appendix 5b for the interrelationships among pressure units.

7. Thermodynamic data for auxiliary substances

In this section are given the basic data for products of combustion and components of air. These are enthalpies of formation, enthalpy differences and heat capacities, all for the ideal gases. The latter two types of data are needed to correct the standard enthalpies of formation at 298.15 K to the various reference conditions of interest in gas technology.

In Table 3a are listed values of C_p°(298.15 K) for each of the auxiliary substances and calculated values of $H^\circ(T_1) - H^\circ(T_2)$, that is $-\{H^\circ(T_2) - H^\circ(T_1)\}$, for the temperature intervals T_1 = 298.15 K; T_2 = 288.15 K; T_2 = 288.71 K (60 °F); and T_2 = 273.15 K. In Table 3b are listed selected values of $\Delta_f H^\circ$(298.15 K) for each of the auxiliary substances and values for $\Delta_f H^\circ$(288.15 K), $\Delta_f H^\circ$(288.71 K), and $\Delta_f H^\circ$ (273.15 K) derived using the data in Table 3a. The sources of the data are discussed in Appendix 7. How the data are interrelated and how the corrections are made are described in Appendix 8.

Table 3. Thermodynamic data for selected (auxiliary) substances

Table 3a. Standard heat capacity at T = 298.15 K and $[H°(298.15\ K) - H°(T_2)]$ for T_2 = 288.15 K, 288.71 K and 273.15 K

Substance (phase)	$C_p^o(298.15\ K)$[a] J·mol^{-1}·K^{-1}	$H°(298.15\ K) - H°(T_2)$[a] kJ·mol^{-1} T_2 = 288.15 K	T_2 = 288.71 K	T_2 = 273.15 K
Ar (g)	20.78	0.208	0.196	0.520
C(c,graphite)	8.53	.083	.081	0.203[b]
CO(g)	29.15	.291	.275	0.728
CO_2(g)	37.12	.369	.348	0.914
H_2(g)	28.83	.288	.272	0.717
H_2O(g)	33.58	.336	.317	0.830[c]
H_2O(ℓ)	75.29	.753	.711	1.888[c]
H_2S(g)	34.10	.340	.321	0.849
He(g)	20.79	.208	.196	0.520
N_2(g)	29.13	.291	.275	0.728
O_2(g)	29.37	.293	.277	0.733
S(c, rhombic)	22.64	.225	.213	---
SO_2(g)	40.06	.399	.376	0.989

[a]Wilhoit, R. C.; [11], except as noted.

[b]DeSorbo, W.; and Tyler, W. W.; [13].

[c]Osborne, N. S.; Stimson, H. F.; Ginnings, D. C.; [12].

Table 3b. Standard enthalpy of formation, at T = 298.15 K, 288.15 K, 288.71 K and 273.15 K

Substance (phase)	$\Delta_f H°(298.15\ K)^a$ / $kJ \cdot mol^{-1}$	$\Delta_f H°(288.15\ K)$ / $kJ \cdot mol^{-1}$	$\Delta_f H°(288.71\ K)$ / $kJ \cdot mol^{-1}$	$\Delta_f H°(273.15\ K)$ / $kJ \cdot mol^{-1}$
Ar(g)	0.0	0.0	0.0	0.0
C(c,graphite)	0.0	0.0	0.0	0.0
CO(g)	-110.53 ± 0.17	-110.59	-110.59	-110.69
CO_2(g)	-393.51 ± 0.13	-393.50	-393.50	-393.49
H_2(g)	0.0	0.0	0.0	0.0
H_2O(g)	-241.814 ± 0.042	-241.715	-241.721	-241.561
H_2O(ℓ)	-285.830 ± 0.042	-286.148	-286.131	-286.634
H_2S(g)	-20.63 ± 1.00	-20.46	-20.47	---
He(g)	0.0	0.0	0.0	0.0
N_2(g)	0.0	0.0	0.0	0.0
O_2(g)	0.0	0.0	0.0	0.0
S(c, rhombic)	0.0	0.0	0.0	0.0
SO_2(g)	-296.81 ± 0.21	-296.69	-296.70	---

[a]Values at 298.15 K were taken from CODATA Bulletin No. 28 and CODATA Special Report 8 [14].

8. Thermodynamic quantities for hydrocarbons - ideal gas, molar basis

In this section are given values for the thermodynamic properties of selected hydrocarbons. The basic data are for the ideal gases and on a molar basis. Those are enthalpies of combustion, heat capacities and enthalpy differences. Combustion data are given at all three reference conditions likely to be used in gas technology.

The ideal-gas values of thermodynamic quantities for the hydrocarbons on a molar basis are listed in Tables 4a and 4b. The sources of the data and derivation of the table are discussed in Appendix 7. The values of $C_p^\circ(298.15\ \mathrm{K})$, $[H^\circ(298.15\ \mathrm{K}) - H^\circ(288.15\ \mathrm{K})]$, $[H^\circ(298.15\ \mathrm{K}) - H^\circ(288.71\ \mathrm{K})]$, and $[H^\circ(298.15\ \mathrm{K}) - H^\circ(273.15\ \mathrm{K})]$, are given for each hydrocarbon in Table 4a. The values of $-\Delta_c H^\circ(298.15\ \mathrm{K})$, $-\Delta_c H^\circ(288.15\ \mathrm{K})$, $-\Delta_c H^\circ(288.71\ \mathrm{K})$, and $-\Delta_c H^\circ(273.15\ \mathrm{K})$ are given in Table 4b. In Appendix 8 is found a discussion of the relationships among quantities in Tables 3a, 3b, 4a and 4b and some illustrative calculations are given.

Table 4. Thermodynamic data for gaseous hydrocarbons (ideal gas, molar basis)

Table 4a. Heat capacity and enthalpy difference between 298.15 K and 288.15 K, 288.71 K and 273.15 K

Substance (phase)	$C_p^o(298.15\ K)$ / $J \cdot mol^{-1} \cdot K^{-1}$	$H°(298.15\ K) - H°(T_2)$ / $kJ \cdot mol^{-1}$, $T_2/K = 288.15$	$T_2/K = 288.71$	$T_2/K = 273.15$
methane	35.71	0.355	0.336	0.882
ethane	52.48	0.519	0.490	1.275
propane	73.59	0.726	0.686	1.779
n-butane	98.44	0.972	0.918	2.384
2-methylpropane (iso-butane)	96.59	0.953	0.900	2.332
n-pentane	119.96	1.185	1.120	2.910
2-methylbutane (iso-pentane)	118.94	1.174	1.109	2.880
2,2-dimethyl-propane (neopentane)	120.96	1.194	1.128	2.923
n-hexane	142.62	1.409	1.331	3.459
2-methyl-pentane	142.35	1.406	1.328	3.458
3-methyl-pentane	140.20	1.384	1.307	3.391
2,2-dimethyl-butane	141.55	1.396	1.319	3.419
2,3-dimethyl-butane	139.56	1.378	1.302	3.380
cyclopropane	55.59	0.546	0.516	1.328
cyclobutane	70.86	0.696	0.658	1.693
cyclopentane	83.11	0.814	0.769	1.971
cyclohexane	105.25	1.033	0.976	2.509
acetylene	44.06	0.437	0.413	1.077
ethylene	43.55	0.423	0.400	1.042
propene	64.41	0.636	0.601	1.561
benzene	85.58	0.841	0.795	2.050

Table 4b. Enthalpy of combustion (in kJ mol^{-1}) at 298.15 K, 288.15 K, 288.71 K and 273.15 K

Substance	$-\Delta_c H°$/kJ mol^{-1}			
	T = 298.15 K	T = 288.15 K	T = 288.71 K	T = 273.15 K
methane	890.31	891.24	891.19	892.65
ethane	1559.84	1561.29	1561.21	1563.49
propane	2219.90	2221.83	2221.72	2224.75
butane	2877.25	2879.61	2879.48	2883.67
2-methylpropane	2868.72	2871.10	2870.97	2874.72
n-pentane	3535.77	3538.60	3538.44	3542.89
2-methylbutane	3528.87	3531.72	3531.55	3563.02
2,2-dimethyl-propane	3514.60	3517.42	3517.26	3521.71
n-hexane	4194.75	4198.04	4197.85	4203.03
2-methyl-pentane	4187.64	4190.94	4190.75	4195.93
3-methyl-pentane	4190.32	4193.64	4193.45	4198.67
2,2-dimethyl-butane	4176.34	4179.65	4179.45	4184.66
2,3-dimethyl-butane	4184.17	4187.49	4187.30	4192.53
cyclopropane	2091.37	2092.87	2092.78	2095.15
cyclobutane	2745.16	2747.19	2747.08	2750.28
cyclopentane	3319.59	3322.19	3322.04	3326.14
cyclohexane	3952.96	3956.02	3955.84	3860.67
ethyne	1299.59	1299.91	1299.86	1300.40
ethene	1410.97	1411.90	1411.85	1413.33
propene	2058.44	2059.85	2059.77	2061.99
benzene	3301.51(API)	3302.94	3302.82	3305.11

9. Standard-state volumetric properties of hydrocarbons

The enthalpy of combustion of unit volume of gaseous hydrocarbon is strongly dependent on the temperature and pressure of the gas. In Table 5 are presented conversion factors (V_m = molar volume and ρ_n = amount of substance (molar density) used to convert standard molar enthalpies of combustion to standard enthalpy of combustion per unit volume of the ideal gas for all the various reference conditions listed in Table 2. The relationships between these quantities are discussed in Appendix 8.

The values of standard volumetric enthalpy of combustion in SI units for the ISO/ANSI/ASTM metric reference conditions are given in Table 6. The relationship by which these values were calculated is:

$$\Delta_c H°(T,p)/\mathrm{kJ\ m^{-3}} = [\Delta_c H°(T)/\mathrm{kJ\ mol^{-1}}]/[V_m^{id}(T)/\mathrm{m^3\ mol^{-1}}], \quad (9.1)$$

or

$$\Delta_c H°(T,p)/\mathrm{kJ\ m^{-3}} = [\Delta_c H°(T)/\mathrm{kJ\ mol^{-1}}] \cdot [\rho_n(T)/\mathrm{mol\ m^{-3}}], \quad (9.2)$$

with

$$V_m^{id} = RT/p \quad (9.3)$$

Either equation may be used. The use of these equations to calculate a standard volumetric enthalpy of combustion is illustrated in the next paragraph.

To convert the standard molar enthalpy of combustion of methane at 288.15 K to the standard volumetric enthalpy of combustion at T = 288.15 K and p = 101.325 kPa, dry basis:

$$\begin{aligned}\Delta_c H°(\mathrm{CH_4},\ 288.15\ \mathrm{K},\ 101.325\ \mathrm{kPa}) &\\ &= (-891.24\ \mathrm{kJ\ mol^{-1}})/(0.023645\ \mathrm{m^3 mol^{-1}}) \\ &= -37693\ \mathrm{kJ\ m^{-3}} \\ &= -37.693\ \mathrm{MJ\ m^{-3}}\end{aligned}$$

This reproduces the value given for methane in Table 6. Equation 9.3 has been used to calculate V_m^{id} for this example and for all later conversions. The values in Table 5 have been rounded so that the uncertainty is in the last decimal place shown.

Table 7 gives the standard volumetric enthalpy of combustion for the U.S. Customary reference conditions: T = 60 °F (288.71 K) and p = 14.73 psia (101.560 kPa). The values are given in U.S. Customary units (Btu ft^{-3}), but also are given in SI units to permit ready comparison with data in Table 6. It must be emphasized that both the temperature and pressure are different for the metric base conditions so that the conversion of values from Table 6 to Table 7 involves other factors than the ratio (Btu ft^{-3}/MJ m^{-3}): 1 MJ m^{-3} = 26.8391924 Btu ft^{-3}. The values in Table 7 are calculated directly from the values in Table 4a by use of the appropriate conversion factors, equation 9.3, as follows:

$$\Delta_c H°(C_aH_b,\ g,\ 288.71\ K,\ 101.560\ kPa)/MJ\ m^{-3} =$$

$$[\Delta_c H°(C_aH_b,\ g,\ 288.71\ K)/MJ\ mol^{-1}]/[V_m(T)/m^3\ mol^{-1}]$$

The process can be illustrated for methane. From Table 4b, $\Delta_c H°(CH_4,\ g,\ 288.71\ K)$ = -891.19 kJ mol^{-1} = -0.89119 MJ mol^{-1}. From Table 5 for the dry gas $V_m(T)$ = 0.023635 $m^3\ mol^{-1}$ at 288.71 K and a pressure of 101.560 kPa.

$$\begin{aligned}\Delta_c H°(CH_4,\ g,\ 288.71\ K,\ 101.560\ kPa,\ dry)\\ &= -(0.89119\ MJ\ mol^{-1})/(0.023635\ m^3\ mol^{-1})\\ &= -37.706\ MJ\ m^{-3}\end{aligned}$$

To convert to units of Btu ft^{-3} multiply this by the conversion factor 1 MJ m^{-3} = 26.8391924 Btu ft^{-3}. The product gives:

$$\begin{aligned}\Delta_c H°(CH_4,\ g,\ 288.71\ K,\ 101.560\ kPa,\ dry)\\ &= -(37.706\ MJ\ m^{-3}) \times (26.8392\ Btu\ ft^{-3}/MJ\ m^{-3})\\ &= -1012.00\ Btu\ ft^{-3}.\end{aligned}$$

reproducing two values in the table.

To find the standard volumetric enthalpy of combustion of the water-saturated gas, use the conversion factor, 0.024054 $m^3\ mol^{-1}$, that is appropriate for the water-saturated gas at 288.71 K and 101.560 kPa. Similar calculations can be made for the other gases (or for mixtures of ideal gases) at any of the reference temperatures.

The calculation of the factors found in Table 5 is discussed in Appendix 8. The vapor pressure of water used for calculating the factors for the water-saturated gas, taken from Wexler's correlation [16], is given in Table A7f in Appendix 7.

Table 5. Molar volume and density at various reference conditions

	DRY GAS			WATER-SATURATED GAS		
p	100 kPa	101.325 kPa	101.560 kPa	100 kPa[a]	101.325 kPa[a]	101.560 kPa[a]
T/K				$V_m^{id}(T)/m^3\ mol^{-1}$ [b]		
273.15	.022711	.022414	.022362	.022850	.022550	.022497
288.15	.023958	.023645	.023590	.024374	.024049	.023993
288.7055+[c]	.024004	.023690	.023635	.024436	.024111	.024054
298.15	.024789	.024465	.024409	.025601	.025255	.025195
				$\rho_n(T)/mol\ m^{-3}$ [b]		
273.15	44.032	44.615	44.719	43.763	44.346	44.450
288.15	41.740	42.293	42.391	41.028	41.581	41.679
288.7055+	41.659	42.211	42.309	40.923	41.475	41.573
298.15	40.340	40.874	40.969	39.062	39.596	39.691

[a] Total pressure, p, which equals $p(CH_4) + p(H_2O)$ where $p(CH_4)$ is the partial pressure of methane (or other fuel gas), and $p(H_2O)$ is the vapor pressure of water [16]. Only $p(CH_4)$ is used in the calculation of V_m^{id}.

[b] Values are rounded. The equation $V_m^{id} = RT/p$ was used to convert data in Table 4 to those in Tables 6 and 7.

[c] 60 °F. 288.706 K used in calculations.

Table 6. Combustion data for selected gaseous hydrocarbons (ideal gas, volumetric basis) in SI units at ISO/ANSI/ASTM reference conditions of temperature and pressure

p = 101.325 kPa; T = 288.15 K[a]

		$-\Delta_c H°/\text{MJ m}^{-3}$	
Substance	Formula	Dry Basis	Wet Basis (sat)[a]
methane	CH_4	37.693	37.059
ethane	C_2H_6	66.031	64.920
propane	C_3H_8	93.967	92.386
n-butane	C_4H_{10}	121.787	119.737
2-methylpropane	C_4H_{10}	121.426	119.383
n-pentane	C_5H_{12}	149.657	147.139
2-methylbutane	C_5H_{12}	149.366	146.853
2,2-dimethylpropane	C_5H_{12}	148.762	146.258
n-hexane	C_6H_{14}	177.547	174.559
2-methylpentane	C_6H_{14}	172.247	174.264
3-methylpentane	C_6H_{14}	177.361	174.376
2,2-dimethylbutane	C_6H_{14}	176.769	173.794
2,3-dimethylbutane	C_6H_{14}	177.101	174.120
cyclopropane	C_3H_6	88.513	87.024
cyclobutane	C_4H_8	116.186	114.231
cyclopentane	C_5H_{10}	150.505	138.140
cyclohexane	C_6H_{12}	167.311	164.495
ethyne	C_2H_2	54.977	54.052
ethene	C_2H_4	59.713	58.708
propene	C_3H_6	87.117	85.651
benzene	C_6H_6	139.691	137.340

[a] $p(H_2O)$ = 1.70532 kPa

Table 7. Combustion data for selected gaseous hydrocarbons (ideal gas, volumetric basis) in SI and U.S. Customary units at ANSI/ASTM/API reference conditions of temperature and pressure p = 101.560 kPa; T = 288.71 K[a]

Substance	Dry Basis		Water-Saturated Basis[b]	
	$-\Delta_c H°$/MJ m^{-3}	$-\Delta_c H°$/Btu ft^{-3}	$-\Delta_c H°$/MJ m^{-3}	$-\Delta_c H°$/Btu ft^{-3}
methane	37.706	1011.99	37.050	994.38
ethane	66.054	1772.83	64.904	1741.98
propane	94.00	2522.87	92.364	2478.97
n-butane	121.83	3269.78	119.71	3212.89
2-methylpropane	121.47	3260.12	119.36	3203.40
n-pentane	149.71	4018.06	147.10	3948.15
2-methylbutane	149.42	4010.24	146.82	3940.47
2,2-dimethylpropane	148.81	3994.01	146.22	3924.52
n-hexane	177.61	4766.85	174.52	4683.92
2-methylpentane	177.31	4758.79	174.22	4675.99
3-methylpentane	177.42	4761.85	174.33	4679.01
2,2-dimethylbutane	176.83	4745.96	173.75	4663.38
2,3-dimethylbutane	177.16	4754.87	174.08	4672.14
cyclopropane	88.544	2376.45	87.003	2335.10
cyclobutane	116.23	3119.44	114.20	3065.16
cyclopentane	140.55	3772.33	138.11	3706.70
cyclohexane	167.37	4492.04	164.46	4413.88
ethyne	54.997	1476.08	54.041	1450.40
ethene	59.735	1603.23	58.695	1575.34
propene	87.147	2338.96	85.631	2298.27
benzene	139.74	3750.50	137.31	3685.25

[a]Molar volumes at 60 °F (288.706 K) of 0.0236355 and 0.0240540 m^3 mol^{-1} have been used to obtain $\Delta_c H°$/MJ mol^{-1}.

[b]$p(H_2O)$ = 1.76734 kPa.

10. Properties of the real gases

The effects of non-ideality on the properties of the real gases are based on the equation of state of the gases as represented by the virial coefficients. The second virial coefficients, $B(T)$, are given for the pure substances in Table 8a at the four temperatures of interest. The derivation of this table and the relationships to the enthalpy and the volume of the real gas are discussed in Appendix 9. In addition, a second degree equation is given there for the virial coefficient of each gas, Table A9a. Table A9c in the Appendix gives the enthalpy increment, $H-H°$, on a molar basis caused by the non-ideality of the gas.

Table 9 gives the real-gas enthalpy of combustion for the hydrocarbons in SI units for the ISO/ANSI/ASTM metric reference conditions of measurement (T = 288.15 K, p = 101.325 kPa) on molar, mass and volume bases. Table 10 gives the real-gas enthalpy of combustion in U.S. Customary units for the ANSI/ASTM/API reference conditions for U.S. Customary units, T = 288.71 K (60°F), and p = 101.560 kPa (14.73 psia), also molar, mass and volume bases. The corrections themselves are included in Tables 11 and 12.

Table 9 is derived directly from Table 4a and the virial coefficients using the cycle (all processes at the same temperature and pressure):

$$\text{real:}\quad C_aH_b(g) + (a + b/4)\ O_2(g) \rightarrow aCO_2(g) + (b/2)\ H_2O(g)$$

$$\downarrow 1 \qquad\qquad \downarrow 2 \qquad\qquad \uparrow 3 \qquad\qquad \uparrow 4$$

$$\text{ideal:}\quad C_aH_b(g) + (a + b/4)\ O_2(g) \rightarrow aCO_2(g) + (b/2)\ H_2O(g)$$

$$\begin{aligned}\Delta_c H(\text{real gas}) = &- [H-H°](C_aH_b,g) - (a+b/4)[H-H°](O_2,g)\\ &+ \Delta_c H° + a[H-H°](CO_2,g)\\ &+ (b/2)[H-H°](H_2O,g)\end{aligned}$$

The calculation is made for methane at 288.15 K and 101.325 kPa as an example. For methane a = 1, b = 4; $(H-H°)$ = -17.0 J mol^{-1} (Table A9c); for oxygen, $H\text{-}H^\circ$ = -8.72 J mol^{-1}; for CO_2, $H\text{-}H^\circ$ = -42.7 J mol^{-1} and for $H_2O(1)$, $H\text{-}H^\circ$ is taken to be zero. $\Delta_c H^\circ(CH_4$, g, 101.325 kPa, 288.15 K) is -891.24 kJ mol^{-1} (Table 4b). From these values:

$$\Delta_c H(CH_4\text{, g, 101.325 kPa, 288.15 K})/\text{kJ mol}^{-1} = -891.24 - 0.0427 - (-0.0170) - 2\,(-0.00872) = -891.2483$$

which rounds to -891.25 kJ mol^{-1}. The adjustment is barely significant in this case.

By a similar procedure, as indicated in Appendixes 8 and 9, $\Delta_c H - \Delta_c H^\circ$ can be calculated for any hydrocarbon and any base conditions of temperature and pressure for which data are given, using Table 4a or 4b and Table A9c of the Appendix.

Table 8. Virial coefficients for pure substances and mixtures

Table 8a. Second virial coefficients, $B(T)$ for pure substances*

Substance	$B(T)/cm^3 mol^{-1}$				
T/K	273.15	288.15	288.71	298.15	δ[a]
methane[b,c] [1][2]	-53.6	-47.0	-46.9	-43.0	± 1
ethyne	---	---	---	---	
ethene [2,5][d]	-167.6	-150.3	-149.3	-139.8	± 1
ethane [2,6][e]	-222.2	-199.1	-198.2	-185.8	± 2
propene	-416	-373	-372	-346	± 40
propane[f]	-464	-415	-413	-383	± 20
cyclobutane	---	---	---	---	
n-butane [2,9][g]	-918	-799	-795	-735	± 20
2-methylpropane [2,9][h]	-895	-738	-735	-682	± 40
cyclopentane	---	---	---	---	
n-pentane[i]	-1680	-1398	-1392	-1270	± 60
2-methylbutane[j]	-1323	-1170	-1115	-1087	± 40
2,2-dimethylpropane[k]	-1205	-1027	-1023	-933	± 35
benzene[l]	-1857	-1613	-1607	-1488	± 30
cyclohexane	-1943	---	---	-1571	± 100[ff]
n-hexane	---	---	---	-1984	± 100[gg]
2-methylpentane[m]	-2054	-1853	-1845	-1712	
3-methylpentane[n]	-2051	-1809	-1798	-1677	± 100[ff]
2,2-dimethylbutane	---	---	---	---	
2,3-dimethylbutane[o]	-1833	-1634	-1627	-1533	± 100[ff]

Table 8a. (Cont'd)

T/K	273.15	288.15	288.71	298.15	δ[a]
carbon monoxide	---	---	---	---	
carbon dioxide [1]	-149.7	-132.3	-132.0	-123.5	± 2
oxygen [1]	-22.0	-18.4	-18.3	-16.1	± 0.1[hh]
nitrogen [1]	-10.5	-7.1	-7.0	-5.1	± 0.1[ii]
helium [1]	+12.0	+11.9	+11.9	+11.8	± 0.05
argon [2,1][p]	-21.7 [1]	-18.2	-18.1	-16.2	± 1
hydrogen [1]	+13.7	+14.0	+14.05	+14.4	± 0.1[ii]
air (CO_2-free, dry) [1]	-13.5	-10.1	-10.0	-8.1	± 0.1
water vapor	-1459.	-1224.	-1217.	-1106.	±60

*Footnotes and references for Table 8 are given in Appendix 9. Unless otherwise indicated, the quoted values are from or are based on those in the compilation of Dymond and Smith [2, appendix 9].

Table 8b. Second virial coefficients, $B_{12}(T)$, for binary mixtures*

Substance	$B_{12}(T)/cm^3 mol^{-1}$				
T/K	273.15	288.15	288.71	298.15	δ
argon + methane[q] [2,13,18,20,21]	-29.0	-23.8	-23.5	-21.0	± 8
carbon dioxide + methane[r] [2,9]	---	---	-62.9	---	± 5
hydrogen + methane[s] [2,9,36]	+6.0	+9.0	+9.2	+11.5	± 5
nitrogen + methane[t] [2,9,38,79]	-22.0	-18.8	-18.5	-17.3	± 5
water + methane[u] [2,3,7]	-85	-71.5	-70.8	-63	± 6
ethene + methane[v] [2,9,24,25,26,27]	-82	-71.0	-70.8	-64.5	± 6
ethane + methane[w] [2,9,28,29,30,31]	-110	-98.6	-98.1	-92.0	± 6
propane + methane[x] [2,9,28,29,31]	-154	-140.5	-140	-132	± 6
n-butane + methane[y] [2,9,28,29,31]	-197	-178.3	-177.7	-167	± 20

Table 8b. (Cont'd)

T/K	273.15	288.15	288.71	298.15	δ
2-methylpropane + methane[z] [2,9]	-177	-159.4	-158.7	-149	± 30
n-pentane + methane[aa] [2,9,29,31,32,33]	-263	-238	-237	-223	± 50
2-methylbutane + methane[bb] [2,9,32]	-246	-221	-220.5	-207	± 50
2,2-dimethylpropane + methane[cc] [2,13,20,34,35]	-216	-184	-183	-170	± 50
n-hexane + methane[dd] [2,29,32]	-318	-289	-288	-277	± 55
2,2-dimethylbutane + methane[ee] [2,32]	-303	-246	-243	-217	± 42

*Footnotes and references are given in Appendix 9.

Table 9. Enthalpy of combustion of the real-gas hydrocarbons on molar, mass, and volume bases; in SI units and at ISO/ANSI/ASTM metric reference condition

P = 101.325 kPa; T = 288.15 K

Substance	$-\Delta_c H$ / kJ mol^{-1}	$-\Delta_c H$ / MJ kg^{-1}	$-\Delta_c H$ / MJ m^{-3}
methane	891.25	55.5537	37.7688
ethane	1561.3	51.922	66.597
propane	2221.8	50.384	95.675
n-butane	2879.4	49.540	126.197
2-methylpropane	2870.9	49.394	125.468
n-pentane	3538.1	49.038	159.726
2-methylbutane	3531.5	48.946	157.583
2,2-dimethlypropane	3517.1	48.748	155.848
n-hexane	---	---	---
2-methylpentane	4190.4	48.626	193.840
3-methylpentane	4193.1	48.657	193.475
2,3-dimethylbutane	4187.1	48.588	191.375
ethene	1411.9	50.328	60.0977
propene	2059.8	48.949	88.4289
benzene	3302.5	42.278	150.785

Table 10. Enthalpy of combustion of the real-gas hydrocarbons on molar, mass, and volume bases; in U.S. Customary units and at ANSI/ASTM/API reference conditions

p = 101.560 kPa; T = 288.71 K

(p = 14.73 psia; T = 60 °F)

Substance	$-\Delta_c H$ / $Btu_{IT} mol^{-1}$	$-\Delta_c H$ / $Btu_{IT} lb^{-1}$	$-\Delta_c H_v$ / $MJ\ m^{-3}$	$-\Delta_c H_v$ / $Btu\ ft^{-3}$
methane	844.69	23882.4	37.7804	1014.00
ethane	1479.7	22321	66.6159	1787.92
propane	2105.7	21660	95.6987	2568.48
n-butane	2729.0	21298	126.218	3387.59
2-methylpropane	2721.0	21235	125.488	3367.99
n-pentane	3353.3	21082	159.714	4286.59
2-methylbutane	3347.0	21042	157.598	4229.81
2,2-dimethlypropane	3333.4	20957	155.858	4183.11
n-hexane	---	---	---	---
2-methylpentane	3971.6	20905	193.828	5202.19
3-methylpentane	3974.2	20918	193.458	5192.28
2,3-dimethylbutane	3968.5	20888	191.378	5136.44
ethylene	1338.2	21637	60.1167	1613.49
propene	1925.3	21043	87.2863	2342.62
benzene	3130.1	18176	150.776	4046.72

11. Volumetric enthalpy of combustion of the real gas

The molar volume of the real gas and the volumetric enthalpy of combustion at ISO/ANSI/ASTM metric reference conditions (p = 101.325 kPa; T = 288.15 K) are given in Table 11. An estimate of the fractional uncertainty of the molar volume is also given. The uncertainty of the molar volume determines the uncertainty in the volumetric enthalpy of combustion.

The molar volume of the real gas and the volumetric enthalpy of combustion at ANSI/ASTM/API U.S. Customary reference conditions are given in Table 12. An estimate of the uncertainty of the molar volume is also given. This factor also gives the approximate contribution of the uncertainty in the volumetric enthalpy of combustion. The molar volume is given both in cubic metres and cubic feet, and the enthalpy of combustion is given in both megajoules per cubic metre and in British thermal units per cubic foot.

The calculation of the real gas molar volume is based on the equation:

$$pV_m/RT = 1 + B(T)/V_m \tag{11.1}$$

for which values of $B(T)$ are taken from Table 8a. This calculation will be illustrated for methane for the conditions p = 101.325 kPa; T = 299.15 K. From Table 8a, B(288.15 K) = -(47.0 ± 1) cm^3 mol^{-1} for methane. The exact quadratic solution of this equation is:

$$V_m/V_m^{id} = \frac{1}{2} + \frac{1}{2}\,(1 + 4B/V_m^{id})^{1/2} \quad , \tag{11.2}$$

where V_m^{id}, the ideal gas volume is RT/P,

$$V_m^{id} = (8.31441 \times 288.15/101325)$$
$$= 0.02364468 \text{ m}^3 \text{ mol}^{-1},$$

or may be obtained from Table 5. To make V_m^{id} commensurate with B, V_m^{id} is converted to 23644.7 cm^3 mol^{-1}. Substitution of these values gives:

$$V_m/23644.7\ \text{cm}^3\ \text{mol}^{-1} = \frac{1}{2} + \frac{1}{2}\,(1 - 4 \times 47.0/23644.7)^{1/2}$$
$$= \frac{1}{2} + \frac{1}{2}\,(0.992049)^{1/2}$$
$$= 0.9980083$$

$$V_m = 23644.7\ \text{cm}^3\ \text{mol}^{-1} \times 0.998008 = 23597.6\ \text{cm}^3\ \text{mol}^{-1}$$
$$V_m = 10^{-6}\ \text{m}^3\ \text{cm}^{-3} \times 23597.6\ \text{cm}^3\ \text{mol}^{-1},$$
$$= 0.023598\ \text{m}^3\ \text{mol}^{-1},$$

in conformity with the value in Table 11.

The volumetric enthalpy of combustion of the real gas is obtained from the molar enthalpy of combustion of the real gas at the same reference conditions (Tables 9 and 10) using the following relationship:

$$\Delta_c H/\text{MJ m}^{-3} = 0.001\ (\Delta_c H/\text{kJ mol}^{-1})/(V_m/\text{m}^3\ \text{mol}^{-1}) \qquad (11.3)$$

This may be illustrated for methane for which $\Delta_c H/\text{kJ mol}^{-1} = -891.248$ (from Tables 4 and 9) and $V_m/\text{m}^3\ \text{mol}^{-1} = 0.0235976$ (from Table 11). The value of:

$$\Delta_c H/\text{MJ m}^{-3} = -891.248\ /\ 0.0235976,$$
$$= -37768.6\ \text{kJ m}^{-3},$$
$$= -37.769\ \text{MJ m}^{-3}.$$

in conformity with Table 9.

The volumetric enthalpy of combustion in Btu ft^{-3} in Table 10 is obtained from the volumetric enthalpy of combustion in MJ m^{-3} in Table 12 using the units Btu_{IT} and foot defined exactly in Table A4 in terms of the joule and the metre.

The molar volumes have an ascribed uncertainty because of the uncertainty in the virial coefficients. This uncertainty is significant, particularly in the cases of the higher hydrocarbons. The uncertainty in the molar volume may be calculated by differentiating equation (11.2) to obtain the relative error:

$$\delta V_m/V_m^{id} = (\delta B/V_m^{id})/(1 + 4B/V_m^{id})^{0.5}$$

and substituting δB from Table 8a (last column). Taking the value 1 cm^3 mol^{-1} (= 10^{-6} m^3 mol^{-1}) for methane from Table 8a, we calculate

$$\begin{aligned}\delta V_m/V_m^{id} &= (1/23645)/(1 + 4\cdot(-47)/23645)^{0.5}\\ &= 3.79 \times 10^{-5}/0.992\\ &= 3.8 \times 10^{-5}\end{aligned}$$

Table 11. Enthalpy correction to the real gas and molar volume, V_m, at ISO/ANSI/ASTM metric reference conditions

p = 101.325 kPa; T = 288.15 K

V_m^{id} = 0.023 644 7

Substance	$\Delta_c H - \Delta_c H°$ / J mol^{-1}	V_m / m^3 mol^{-1}	$\delta V_m / V_m$[a]
methane	-8.3	0.0235976	4×10^{-5}
ethane	7.0	0.0234439	8×10^{-5}
propane	54.5	0.0232222	8.6×10^{-4}
n-butane	154.9	0.0228167	8.6×10^{-4}
2-methylpropane	191.9	0.0228815	1.8×10^{-3}
n-pentane	482.3	0.0221511	2.7×10^{-3}
2-methylbutane	260.1	0.0224102	1.8×10^{-3}
2,2-dimethylpropane	284.3	0.0225677	1.5×10^{-3}
n-hexane	---	---	---
2-methylpentane	473.6	0.0216181	9.2×10^{-4}
3-methylpentane	482.6	0.0216727	---
2,3-dimethylbutane	363.6	0.0218792	---
ethene	-12.0	0.0234936	4×10^{-5}
propene	32.1	0.0232935	---
benzene	428.0	0.0219024	1.4×10^{-3}

[a]Relative error in the real-gas molar volume.

Table 12. Enthalpy correction to the real gas and molar volume, V_m, at ANSI/ASTM/API U.S. Customary reference conditions

P = 101.560 kPa; T = 288.71 K

(V_{id} = 0.023 635 4 $m^3\ mol^{-1}$; 1 ft^3 = 0.028 316 847 m^3)

Substance	$\Delta_c H - \Delta_c H^o$ / $J\ mol^{-1}$	V_m / $m^3\ mol^{-1}$	V_m / ft^3	$\delta V_m/V_m$
methane	-8.0	0.023 5889	0.833 034	4×10^{-5}
ethane	7.4	0.023 4359	0.827 631	8×10^{-5}
propane	55.2	0.023 2152	0.819 837	8.6×10^{-4}
n-butane	181.7	0.022 8121	0.805 602	8.6×10^{-3}
2-methylpropane	186.7	0.022 8770	0.807 894	1.8×10^{-3}
n-pentane	476.3	0.022 1519	0.782 287	2.7×10^{-3}
2-methlybutane	261.3	0.022 4069	0.791 292	1.8×10^{-3}
2,2-dimethyl-propane	285.3	0.022 5652	0.796 883	1.5×10^{-3}
n-hexane	---	---	---	---
2-methylpentane	476.9	0.021 6185	0.763 450	9.2×10^{-4}
3-methylpentane	480.9	0.021 6737	0.765 399	---
2,3-dimethyl-butane	361.9	0.021 8778	0.772 607	---
ethene	-11.7	0.023 4854	0.829 379	4×10^{-5}
propene	33.0	0.023 5982	0.833 362	---
benzene	425.5	0.021 9026	0.773 483	1.4×10^{-3}

12. Calculating the heating values of gas mixtures

The heating value of any fuel gas mixture can be calculated from the molecular composition of the gas and information about the heating values and volumetric behavior of the individual components. It is impractical to calculate heating values for all probable compositions and so the information presented here is limited to procedures for making the calculations.

<u>Composition</u>. It is essential that the composition of the gas be known in order to use these procedures. The composition values must be identifiable as mole fraction or mass fraction of each component and these fractions must account for all of the gas.

The most useful description of the composition is the mole fraction, x, and most of the procedures described here are based on this parameter. The mole fraction of component i is $x(i)$, where i has the values 1 to n, and n is the total number of components. It is necessary that:

$$x(1) + x(2) + \ . \ . \ . + x(n) = 1. \qquad (12.1)$$

Methods of analysis based upon calibration with mixtures of known composition give results in the same terms as the calibration sample. Therefore the meaning of the composition of the calibration sample should be unambiguous if the results of analyses are to be used for the calculation of heating value. Volumetric analyses of gases, give volume fractions of the components that approximate the mole fractions. It should be realized however that volumes of gases are not precisely additive when the gases are mixed, and so volume fraction is somewhat ambiguous. Masses are additive and amounts of substance (moles) are additive and so compositions of gases stated as mass fraction or mole fraction are unambiguous.

Three procedures for calculating heating value based on information in this document will be described:

(1) The heating value of an ideal gas mixture.

(2) The heating value of a real gas mixture, neglecting molecular interactions between different substances.

(3) The heating values of real gas mixtures including molecular interactions between different substances.

12.1 Heating value of an ideal gas mixture

The composition of the gas mixture in terms of the mole fractions $x(i)$ of the individual substances present is presumed to be given, and the sum of the $x(i)$ is unity (equation 12.1).

The enthalpy of combustion of the ideal gas mixture is calculated by adding the molar enthalpies of combustion of the individual components weighted according to their mole fractions using the equation:

$$\Delta_c H^\circ_m(\text{mixture}) = x(1)\Delta_c H^\circ_m(1) + x(2)\Delta_c H^\circ_m(2) + \ldots + x(n)\Delta_c H^\circ_m(n), \quad (12.2)$$

where $\Delta_c H^\circ_m$ is the enthalpy of combustion per mole, of the ideal gas. The enthalpies of combustion are taken from Table 4b. By summation of terms as illustrated in Table 13 for a typical gas, the ideal-gas heating value is calculated.

For the example, the value found by this procedure is $\Delta_c H^\circ_m(\text{mixture}) = -922.01\ \text{kJ mol}^{-1}$. Using the appropriate molar volume from Table 5, this can be converted as shown in Table 13 to $\Delta_c H^\circ_v = -38.994\ \text{MJ m}^{-3}$ or $= -1046.6\ \text{Btu ft}^{-3}$, where $\Delta_c H^\circ_v$ is the enthalpy of combustion of unit volume of the gas mixture (dry).

For ideal gases the volume fractions are proportional to the mole fractions, and so an alternative approach may be used. Heating value per unit volume $\Delta_c H^\circ_v$ can be taken from Table 6, and the same form of equation can be used.

$$\Delta_c H^\circ_v(\text{mixture}) = x(1)\Delta_c H^\circ_v(1) + x(2)\Delta_c H^\circ_v(2) + \ldots + x(n)\Delta_c H^\circ_v(n) \quad (12.3)$$

As shown in Table 13 these data lead to the same result.

For U.S. Customary reference conditions, Table 4b and Table 5, or Table 7, may be used in the same way using either alternative approach.

Table 13. Sample calculation of enthalpy of combustion of a gaseous mixture assuming ideal gas behavior

(p = 101.325 kPa; T = 288.15 K)

(V_m = 0.023 6447 m^3 mol^{-1})

Component (i)	M(i)[a]	x(i)[a]	$\frac{-\Delta_c H^\circ_m(i)}{kJ\ mol^{-1}}$	$\frac{-x(i)\Delta_c H^\circ_m(i)}{kJ\ mol^{-1}}$	$\frac{-\Delta_c H^\circ_V(i)}{MJ\ m^{-3}}$	$\frac{-x(i)\Delta_c H^\circ_V(i)}{MJ\ m^{-3}}$
CH_4	16.043	0.9000	891.24	802.116	37.693	33.9237
C_2H_4	28.054	0.0037	1411.90	5.224	59.713	0.2209
C_2H_6	30.070	0.0550	1561.29	85.871	66.032	3.6318
N_2	28.0134	0.0313	0.0[b]	0.0	0.0	0.0
n-C_4H_{10}	58.123	0.0100	2879.61	28.796	121.787	1.2179
Sums		1.0000		$-\Delta_c H^\circ_m$ = 922.007		$-\Delta_c H^\circ_V$ = 38.9943

$$-\Delta_c H^\circ_m \text{ (mixture)} = 922.007 \text{ kJ mol}^{-1}$$

$$\div\ 0.023\ 6447 \text{ m}^3 \text{ mol}^{-1} = 38\ 994.2 \text{ kJ m}^{-3}$$

$$-\Delta_c H^\circ_V \text{ (mixture)} = 38\ 994.2 \text{ kJ m}^{-3} \cdot 26.839\ 192 \text{ (Btu/ft}^3\text{)/(MJ m}^{-3}\text{)}$$

$$= 1046.6 \text{ Btu ft}^{-3}$$

[a] M(i) is molecular weight and χ(i) is mole fraction.

[b] Molecular nitrogen is the defined combustion product. Corrections are made for nitrogen oxides in the calorimetric experiments.

12.2 Heating value of a real gas mixture, neglecting interactions between different substances

The composition of the gas mixture in terms of the mole fractions $x(\mathrm{i})$ of the individual substances present or in terms of the mass fractions $w(\mathrm{i})$ of the individual substances present is presumed to be known and $\Sigma x(i)$ is unity (equation 12.1) or $\Sigma w(i)$ is unity (equation 12.4).

$$w(1) + w(2) + \ldots + w(n) = 1 \qquad (12.4)$$

The enthalpy of combustion of the real gas mixture on a molar basis, $\Delta_c H_m$(mixture) is calculated by the equation:

$$\Delta_c H_m(\text{mixture}) = x(1)\Delta_c H_m(1) + x(2)\Delta_c H_m(2) + \ldots + x(n)\Delta_c H_m(n). \qquad (12.5)$$

Similarly the enthalpy of combustion of the real gas mixture on a mass basis, $\Delta_c H_w$(mixture) is calculated by the equation:

$$\Delta_c H_w(\text{mixture}) = w(1)\Delta_c H_w(1) + w(2)\Delta_c H_w(2) + \ldots + w(n)\Delta_c H_w(n). \qquad (12.6)$$

Values for $\Delta_c H_m(i)$ or $\Delta_c H_w(i)$ are obtained from Table 9 for ISO/ANSI/ASTM metric reference conditions and from Table 10 for ANSI/ASTM/API U.S. Customary reference conditions.

The enthalpy of combustion of the real gas mixture on a volumetric basis, $-\Delta_c H_v$(mixture), is obtained from $-\Delta_c H_m$(mixture) using the relationship

$$-\Delta_c H_v(\text{mixture}) = -\Delta_c H_m(\text{mixture})/V_m(\text{mixture}). \qquad (12.7)$$

The value for $-\Delta_c H_v$(mixture) to use in equation (12-7) is obtained from equation (12-5). The value of V_m(mixture) is obtained from equation (12-8).

$$V_m(\text{mixture}) = x(1)V_m(1) + x(2)V_m(2) + \ldots + x(n)V_m(n). \qquad (12.8)$$

This equation assumes that volumes of real gases are additive in mixtures. These calculations for a simple mixture are illustrated in Table 14.

Table 14. Sample calculation of enthalpy of combustion of a real-gas mixture assuming no interactions between different substances

(p = 101.325 kPa; T = 288.15 K)

Component (i)	M(i)	x(i)	$V_m(i)$ / $dm^3\ mol^{-1}$ (Table 11)	$-\Delta_c H_m(i)$ / $kJ\ mol^{-1}$ (Table 9)	$-x(i)\Delta_c H_m(i)$ / $kJ\ mol^{-1}$	$x(i)V_m(i)$ / $dm^3\ mol^{-1}$
CH_4	16.043	0.9000	23.5976	891.25	802.125	21.2378
C_2H_4	28.054	0.0037	23.4936	1411.9	5.224	0.0869
C_2H_6	30.070	0.0550	23.4439	1561.3	85.872	1.2894
N_2	28.0134	0.0313	23.6376	0.0[a]	0.0	0.7389
$n\text{-}C_4H_{10}$	58.123	0.0100	22.8167	2879.4	28.794	0.2282
Sums		1.0000			$-\Delta_c H_m$ = 922.015	V_m = 23.5821

$$-\Delta_c H_v \text{ (mixture)} = -\Delta_c H_m \text{ (mixture)}/V_m\text{(mixture)}$$
$$= 0.922\ 015/0.023\ 5821$$
$$= 39.098 \text{ MJ m}^{-3}$$

This is greater than $-\Delta_c H_v^\circ$(mixture) (38.994 MJ m^{-3} from Table 13) on the assumption of ideal-gas behavior by a factor of 1.0027, or different by 2.7 parts in 1000.

[a]See note b, Table 13.

12.3 Heating value of a real gas mixture including molecular interactions between different substances

The composition of the gas mixture in terms of the mole fractions $x(i)$ of the individal substances present, or in terms of the mass fractions $w(i)$ of the individual substances present, is presumed to be known, and $\Sigma x(i)$ is unity (equation 12.1) or $\Sigma w(i)$ is unity (equation 12.4).

The calculation of the heating value involves five steps: (1) the calculation of the ideal gas molar heating value of the mixture using equation (12.2); (2) the calculation of the virial coefficient of the gas mixture and its temperature derivative using equations taken from Appendix 9; (3) calculation of the molar volume of the real gas mixture based upon the virial coefficient of the gas mixture from Step 2; (4) adjustment of the molar heating value for the term $H - H^{\circ}$ based on the virial coefficient of the gas mixture and its derivative; (5) calculation of the heating value on a mass basis and the volumetric heating value of the real gas mixture. The molar heating value $\Delta_c H_m$(mixture) can be converted to the heating value on a mass basis $\Delta_c H_w$(mixture) by use of the mass fractions of the substances in the gas. From the molar volume calculated in step 3, the molar enthalpy of combustion can be converted to the volumetric enthalpy of combustion, $\Delta_c H_v$(mixture).

This calculation procedure is considered to be the most accurate of those presented. It is applicable to both dry and humid gases, including the water-saturated gas.

Step 1. Calculation of heating value of the ideal gas mixture. This step is carried out as described in Section 12.1 and illustrated in Table 13.

Step 2. Calculation of the second virial coefficient B(mixture) of the real gas mixture, and its derivative dB/dT. As described in Appendix 9, the second virial coefficient B(mixture) is a function of T and of the virial coefficients of the components and of the virial coefficients of the binary mixtures of the components. From Appendix 9 we use the simplified equation (12.9) for which data are given in Tables 8a and 8b.

$$B(\text{mixture}) = [x(1)]^2 B(1) + [x(2)]^2 B(2) + \ldots + [x(n)]^2 B(n) + 2x(1)x(2)B(1,2) + 2x(1)x(3)B(1,3) + \ldots 2x(1)x(n)B(1,n) \quad (12.9)$$

Component 1 is taken to be methane in every case (See Appendix 8). This equation is applicable only to natural gas containing methane as the major component. For other gases See Appendix 9.

Using values of $x(i)$ from Step 1, values of $B(i)$ from Table 8a and values of $B(1,i)$ from Table 8b, calculate B(mixture) using equation (12.9). The values of $B(i)$ and $B(1,i)$ must be those for the temperature at which the heating value is desired. For calculations at temperatures other than those listed in Table 2, see the procedures described in Section 10 and Appendix 9. Calculate $dB(\text{mixture})/dT$ using equation (12-10)

$$\begin{aligned} dB(\text{mixture})/dT = {} & [x(1)]^2[dB(1)/dT] + [x(2)]^2[dB(2)/dT] \\ & + \ldots + [x(n)]^2[dB(n)/dT] \\ & + 2x(1)x(2)[dB(1,2)/dT] + 2x(1)x(3)[dB(1,3)/dT] \\ & + \ldots + 2x(1)x(n)[dB(1,n)/dT]. \end{aligned} \quad (12.10)$$

For equation (12.10) obtain values of $dB(i)/dT$ and $dB(1,i)/dT$ at the desired temperature from Table A9b in the appendix. The calculation of

$dB(\text{mixture})/dT$ may be omitted if step 4, calculation of the value $H - H^\circ$, is omitted.

Step 3. Calculate $V_m(\text{mixture})$ for the gas mixture using equation (12.11).

$$V_m(\text{mixture})/V_m(\text{ideal}) = \frac{1}{2} + \frac{1}{2}\,[1 + 4B(\text{mixture})/V_m^{id}]^{1/2} \qquad (12.11)$$

where V_m^{id} may be taken from Table 5 or may be calculated as $V_m^{id} = RT/p$, and $B(\text{mixture})$ is obtained from equation (12.9).

Step 4. Correct to the real gas by calculating $H - H^\circ$ for the gas mixture using equation (12.12)

$$H - H^\circ = (RT/V_m)[B - T(dB/dT)] \qquad (12.12)$$

For this equation use $B(\text{mixture})$ and $dB(\text{mixture})/dT$ from step 2, $V_m(\text{mixture})$ from step 3 and T, the selected temperature for which the heating value is required. Calculate $\Delta_c H_m - \Delta_c H^\circ_m$ as described in Section 10. In order to do this, calculate the equivalent molecular formula of the gas mixture C_aH_b to be used in the equation:

$$C_aH_b + (a + b/4)O_2(g) = a\ CO_2(g) + (b/2)H_2O(l).$$

Step 4 and the required calculation of $dB(\text{mixture})/dT$ can be omitted with errors not exceeding an estimated 50 J mol^{-1}.

Step 5. Calculate $\Delta_c H_m(\text{mixture})$, and $\Delta_c H_v(\text{mixture})$ using equations (12.13) and (12.14)

$$\Delta_c H_m(\text{mixture}) = \underbrace{\Delta_c H_m^\circ(\text{mixture})}_{\text{Step 1}} + \underbrace{(\Delta_c H_m - \Delta_c H_m^\circ)(\text{mixture})}_{\text{Step 4}} \qquad (12.13)$$

$$\underbrace{\Delta_c H_V(\text{mixture})}_{\text{Step 5}} = \Delta_c H_m(\text{mixture})/\underbrace{V_m(\text{mixture})}_{\text{Step 3}} \qquad (12.14)$$

(or alternatively obtain $\Delta_c H_m^\circ(\text{mixture})/V_m(\text{mixture})$ as described in Step 4).

13. Uncertainties

The following sources of uncertainty are considered in this document:

(1) Uncertainty in the standard molar enthalpy of combustion of the pure substance at reference temperature T = 298.15 K.

(2) Uncertainty introduced by conversion of data at the reference temperature 298.15 K to T = 288.15 K, 288.71 K, and 273.15 K, for the pure substances.

(3) Uncertainty introduced by the conversion of the standard molar enthalpy of combustion to standard specific enthalpy of combustion for the pure substances (mass basis).

(4) Uncertainty introduced by conversion of the standard molar enthalpy of combustion to the standard volumetric enthalpy of combustion of the pure substances.

(5) Uncertainty in the relation of the molar or specific enthalpy of combustion of the real gas to that of the ideal gas for the pure substances.

(6) Uncertainty in the relation of the volumetric enthalpy of combustion of the real gas to that of the ideal gas for the pure substances.

(7) Uncertainty in the enthalpic effects of mixing of components of a gas mixture.

(8) Uncertainty in the volumetric effects of mixing of components of a gas mixture.

The inaccuracy in the enthalpy of combustion of a given quantity of gas depends upon errors in actual measurements of mass or volume, temperature, pressure, and composition of the gas under consideration. The detailed consideration of these errors is considered to be beyond the scope of this document.

The uncertainties in the source data are included in various tables: (a) Uncertainties of enthalpies of formation of auxiliary substances, Table 3b; (b) Uncertainties in enthalpies of combustion, heat capacities and enthalpy increments, Table 15; (c) Uncertainties in virial coefficients, Tables 8a and 8b; (d) Uncertainties in physical constants Table 1 and later in this section. In addition some discussions of these uncertainties are given in Appendixes 7 and 10.

Propagation of uncertainties.

The propagation of uncertainties in the calculation of the quantities in this document is carried out using the equation recommended by the IUPAC Commission on Thermodynamics [17].

For the function:

$$F = F(X,Y,Z) \tag{13.1}$$

that is a function of three independent variables, the estimated uncertainty s_F in F is given by:

$$(s_F)^2 = (\partial F/\partial X)^2\{s(X)\}^2 + (\partial F/\partial Y)^2\{s(Y)\}^2 + (\partial F/\partial Z)^2\{s(Z)\}^2 \quad . \tag{13.2}$$

The application of this propagation-of-error equation is discussed in Appendix 10 for particular classes of functions important in this document.

The variables are considered to be independent in each step of calculation except in the case of fuel mixtures for which there is a constraint:

$$\Sigma x_i = 1 \quad . \tag{13.3}$$

The procedure for reducing this set of variables to an independent set is discussed in Appendix 10 in connection with the propagation of errors for virial coefficients of mixtures.

The calculation of desired quantities from observed data follows a logical sequence in this document. The flow charts of the calculations showing many of the equations used are given in figures 1 and 2 which reflect the order used in the presentation of the material in the main text to this point. The calculation of uncertainties and their propagation is carried out stepwise, as listed above, the uncertainty of each quantity incorporating the uncertainties in the variables involved, for which the uncertainties would have been calculated in a previous step.

Table 15. Estimated uncertainties in thermodynamic properties

Substance	$s\{\Delta_c H^\circ(298.15\ K)\}$ kJ mol^{-1}	$10^4 s_c/\Delta_c H^\circ$	$s\{Cp(298.15\ K)\}$ J mol^{-1}K^{-1}	$s\{H(298.15\ K) - H(T_2)\}$ kJ mol^{-1} T_2 = 288.15 K	T_2 = 273.15 K
methane	0.62	7.0	0.42	0.004	0.010
ethane	1.01	6.5	0.42	0.004	0.010
propane	1.02	4.6	0.34	0.003	0.009
n-butane	1.44	5.0	0.42	0.004	0.010
2-methylpropane	1.44	5.0	0.34	0.003	0.009
n-pentane	0.46	1.3	0.50	0.005	0.013
2-methlybutane	0.46	1.3	0.50	0.005	0.013
2,2-dimethylpropane	0.50	1.4	0.50	0.005	0.013
n-hexane	0.63	1.5	0.58	0.006	0.015
2-methylpentane	1.05	2.5	0.58	0.006	0.015
3-methylpentane	1.05	2.5	0.58	0.006	0.015
2,2-dimethylbutane	0.96	2.3	0.66	0.007	0.017
2,3-dimethylbutane	0.92	2.2	0.66	0.007	0.017
cyclopropane	0.54	2.8	0.34	0.003	0.009
cyclobutane	0.50	1.8	0.42	0.004	0.010
cyclopentane	0.71	2.1	0.42	0.004	0.010
cyclohexane	0.63	1.6	0.50	0.005	0.013
ethyne	0.63	4.8	0.42	0.004	0.010
ethene	0.42	3.0	0.42	0.004	0.010
propene	0.67	3.2	0.42	0.004	0.010
benzene	0.54	1.6	0.60	0.006	0.015
oxygen	-	-	0.04	4×10^{-4}	0.001
carbon dioxide	0.13	-	0.42	0.004	0.010
water (liquid)	0.042	-	0.005	5×10^{-5}	1.3×10^{-4}
carbon	-	-	0.02	2×10^{-4}	5×10^{-4}

In order to place the overall uncertainties of the values at various stages listed above in proper perspective, the sources of uncertainty are first discussed for specific factors:

(1) Relative atomic masses (atomic weights)

On the basis that the uncertainties in the atomic masses of the elements have the values given in Table A3d the uncertainties in the molecular weights of the compounds of interest are as follows, where *s* is the uncertainty in atomic weight units and

s/M is the fractional uncertainty.

Substance	10^4 *s*	10^4 *s/M*
	atomic mass unit	
CH_4	6.2	0.4
CH	3.8	0.3
CO_2	9	0.2
H_2O	4.6	0.3

The values for CH_4 and CH represent the extremes of C:H ratios encountered in this document, and relative uncertainties for other hydrocarbons will fall in between. The relative uncertainty introduced by those of the atomic masses is 3 or 4 x 10^{-5}. The calculation of these values by simple addition of uncertainties, and an alternative calculation based on quadratic addition of uncertainties are shown in Table A5d, along with some comments about the sources of the estimates.

(2) Uncertainty in the gas constant *R*

The uncertainty in *R* is 0.00026 in 8.31441 J mol^{-1} K^{-1} or a relative uncertainty of 31 x 10^{-6}.

(3) Uncertainty in the temperature scale

The practical temperature scale is exactly equal to the thermodynamic temperature scale at T = 273.15 K. At T near 294 K, the international practical temperature scale differs from the thermodynamic temperature scale by amounts estimated by Guildner and Edsinger [18] at about 0.0025 to 0.0030 K and at T near 315 K by about 0.0065 to 0.0082 K, with deviations decreasing to very small values as T approaches 273.15 K. From these we can estimate that at T = 298.15 K the error will be about 0.004 K, which corresponds to a fractional error in temperature of 1.3×10^{-5}. This is the maximum error that would be expected in the temperature scale in the range 273.15 K to 298.15 K. In addition, by rounding 288.7055 K (60 °F) to 288.71 K an additional error of 0.0045 K can be introduced if this approximation is made, and additional relative error of 1.6×10^{-5}. (Usually, we have avoided this by using 288.706 K).

(4) Relative uncertainties in the ideal gas molar volume V_m^{id}

We use equation (25) Appendix 10 to calculate the relative uncertainties $s^{id}_{V(T,p)}/V^{id}_{T,p}$. For defined reference conditions p is defined constant and so s_p = 0; T can be considered as defined constant or as defined by IPTS-68 which differs from T (thermodynamic) as described in paragraph 3. Thus s can be taken as zero or s/T can be taken as 0 at T = 273.15 K, and 1.3×10^{-5} at other temperatures used in this document. For s_R we take the uncertainty stated above for R, 26×10^{-5} J mol^{-1} K^{-1}, or $s_R/R = 31 \times 10^{-6}$. Using these data, and assuming the additive worst case of calculations using T = 288.70555 rounded to 288.71 and an error of 1.3×10^{-5} in the deviation of T at 60 °F, we obtain the relative errors in molar volume tabulated in the last column below, valid at all standard pressures at the temperatures indicated.

T/K	$10^6 s_R/R$	$10^6 s_T/T$	s_p/p	$s^{id}_{V(T,p)}/V^{id}_{p,T}$
273.15	31	0	0	31×10^{-6}
288.15	31	8	0	32×10^{-6}
288.71	31	29	0	42×10^{-6}
298.15	31	13	0	34×10^{-6}

For the equations to be used for calculation of uncertainties of types 2 through 8, listed at the beginning of this section see the section on propagation of uncertainties in Appendix 10.

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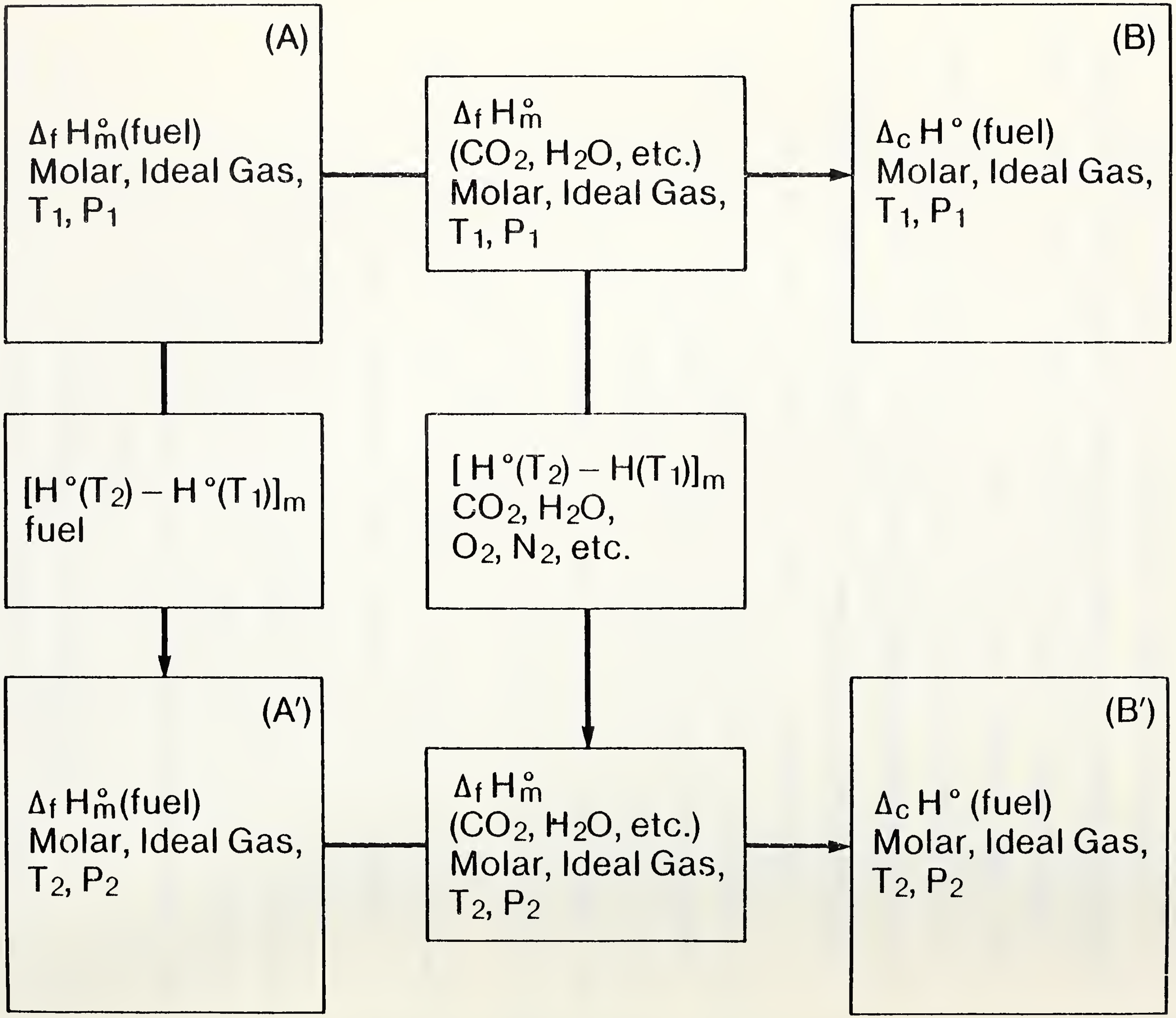
(A)
$\Delta_f H^\circ_m$(fuel)
Molar, Ideal Gas,
T_1, P_1
$\Delta_f H^\circ_m$
(CO_2, H_2O, etc.)
Molar, Ideal Gas,
T_1, P_1
(B)
$\Delta_c H^\circ$ (fuel)
Molar, Ideal Gas,
T_1, P_1
$[H^\circ(T_2) - H^\circ(T_1)]_m$
fuel
$[H^\circ(T_2) - H(T_1)]_m$
CO_2, H_2O,
O_2, N_2, etc.
(A′)
$\Delta_f H^\circ_m$(fuel)
Molar, Ideal Gas,
T_2, P_2
$\Delta_f H^\circ_m$
(CO_2, H_2O, etc.)
Molar, Ideal Gas,
T_2, P_2
(B′)
$\Delta_c H^\circ$ (fuel)
Molar, Ideal Gas,
T_2, P_2

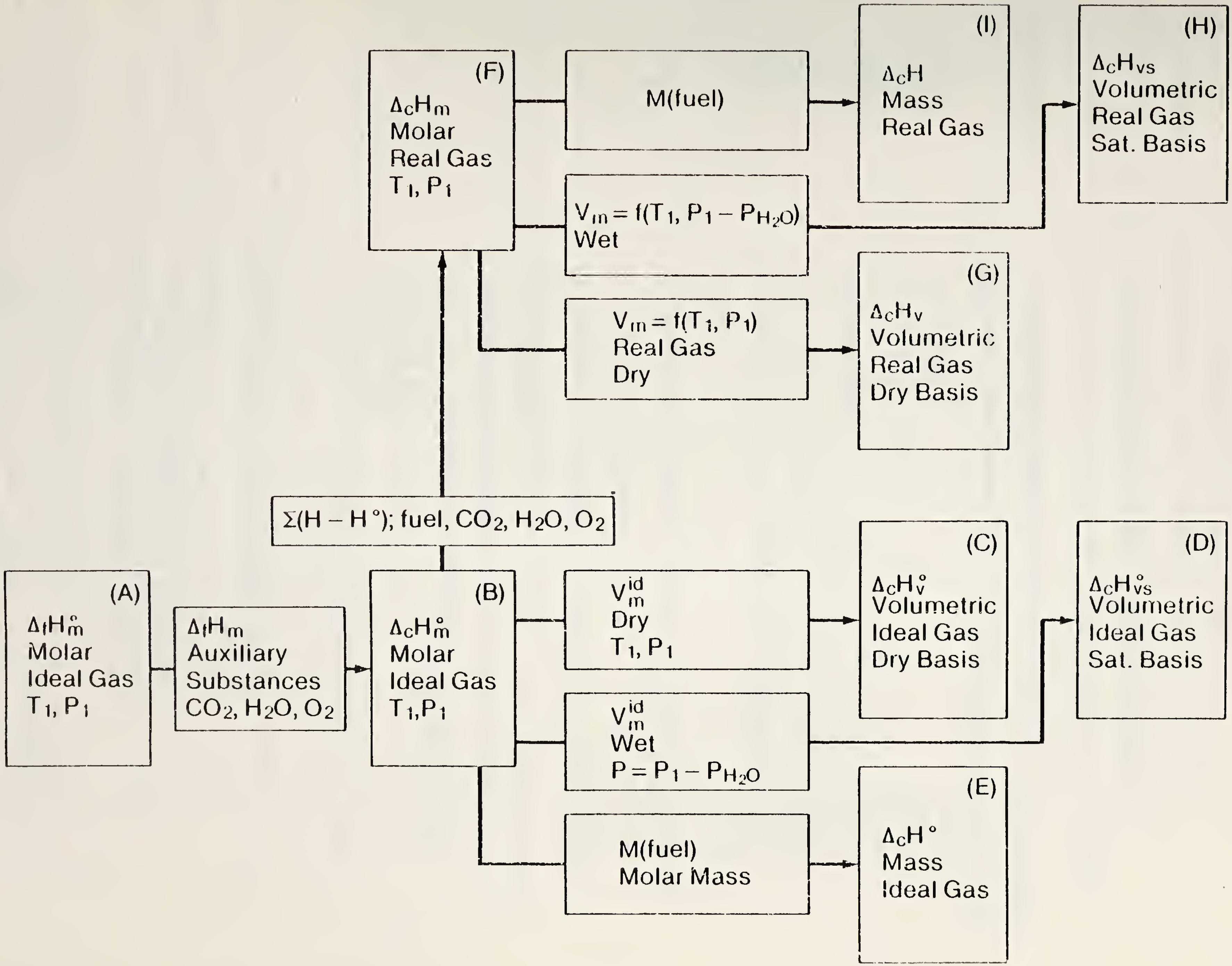
(A)
Δ_f H°_m
Molar
Ideal Gas
T_1, P_1
Δ_f H_m
Auxiliary
Substances
CO_2, H_2O, O_2
(B)
Δ_c H°_m
Molar
Ideal Gas
T_1, P_1
Σ(H − H°); fuel, CO_2, H_2O, O_2
(F)
Δ_c H_m
Molar
Real Gas
T_1, P_1
M(fuel)
V_m = f(T_1, P_1 − P_H2O)
Wet
V_m = f(T_1, P_1)
Real Gas
Dry
(I)
Δ_c H
Mass
Real Gas
(H)
Δ_c H_vs
Volumetric
Real Gas
Sat. Basis
(G)
Δ_c H_v
Volumetric
Real Gas
Dry Basis
V^id_m
Dry
T_1, P_1
V^id_m
Wet
P = P_1 − P_H2O
M(fuel)
Molar Mass
(C)
Δ_c H°_v
Volumetric
Ideal Gas
Dry Basis
(D)
Δ_c H°_vs
Volumetric
Ideal Gas
Sat. Basis
(E)
Δ_c H°
Mass
Ideal Gas

Figure 2

Appendix 1. Proposed composition limits

Table A1 gives composition limits suggested by ASTM Committee D-3 [1] on Gaseous Fuels in a proposed model specification for pipeline quality gas.

Table A1. Proposed composition limits for pipeline quality natural gas

Composition	Minimum Value	Maximum Value
Major and Minor Components	Mole fraction	
Methane	0.65	1.00
Ethane	--	0.14
Propane	--	0.05
Butanes	--	0.02
Pentanes and Heavier	--	0.005
Nitrogen and other Inert Gases	--	0.18
Carbon Dioxide	--	0.03
Hydrogen	--	0.05
Total Unsaturated Hydrocarbons	--	0.005
Carbon Monoxide	--	0.001
Oxygen	--	0.001 (1000×10^{-6})
Trace Components	mg/m^3	
Hydrogen Sulfide	--	5.7
Mercaptan Sulfur	--	11.5
Total Sulfur	--	22.9
Water Vapor	--	110.

Other Characteristics	Minimum Value	Maximum Value
Heating value under standard conditions[a]		
Gross, saturated	35.4 MJ m^{-3} (950 Btu ft^{-3})	42.8 MJ m^{-3} (1150 Btu ft^{-3})
Gross, dry	36.0 MJ m^{-3} (967 Btu ft^{-3})	43.6 MJ m^{-3} (1170 Btu ft^{-3})
Relative density (specific gravity)	0.530	0.790

Liquids: The gas shall be free of water and hydrocarbons in liquid form at the temperature and pressure at which it is delivered to a purchaser.

Solids: The gas shall be free of solid particulate substances in amounts deleterious to the materials normally encountered in transportation and utilization of the gas.

Gases: The gas shall be free of other gases that could adversely effect the transportation or utilization of the gas.

[a] factor 1 MJ m^{-3} = 26.839 192 Btu ft^{-3} under identical temperature and pressure.

[1] Anon; "New standard: D4087. Specification for pipeline quality natural gas"; ASTM Standardization News (Dec. 1981) 9, [12], p. 38E.

Appendix 2. Symbols

Table A2. Thermodynamic symbols used in this document

T	thermodynamic temperature (Kelvin scale)
p	pressure (absolute)
(g)	gas phase
(l)	liquid phase
(c)	crystal phase
ρ_n	concentration or amount-of-substance density (amount of substance per unit volume, i.e., moles per unit volume)
$\rho_n(CH_4, dry)$	concentration or amount of substance density of methane with no water present
$\rho_n(CH_4, sat)$	concentration or amount of substance density of methane when saturated with water vapor
$c(H_2O$, id g)	concentration of saturated water vapor, ideal gas
V_m^{id}	molar volume of ideal gas in standard state
V_m	molar volume of non-ideal gas
r(sat/dry)	ratio of concentration of fuel in saturated gas to concentration of fuel in dry gas
Q	heat released per unit quantity of fuel in a specified process
Q(total)	total heat of reaction, i.e. with fuel in gaseous state and water formed as a liquid
H_T° or $H^\circ(T)$	standard enthalpy at temperature T
H_T or $H(T)$	enthalpy in a non-standard state at temperature T, e.g. enthalpy of the real gas

$H(C_aH_b$, g, 298.15 K, 101.325 kPa)	enthalpy in a non-standard state of the substance C_aH_b at T = 298.15 K, p = 101.325 kPa
H(state 2) - H(state 1)	enthalpy difference or increment, written here for non standard states. Measurable, while H(state) is not
$\Delta_f H°$	standard enthalpy of formation from the elements
$\Delta_f H$	enthalpy of formation from the elements in a non-standard state
$\Delta_f H°(T)$	standard enthalpy of formation at temperature T
$\Delta_f H°(C_aH_b$, g, 298.15 K)	standard enthalpy of formation of the gaseous substance C_aH_b at T = 298.15 K
$\Delta_c H°$	standard enthalpy of combustion (ideal gas)
$\Delta_c H$	enthalpy of combustion (real gas)
$\Delta_c H°(T)$	standard enthalpy of combustion at temperature T
$\Delta_c H(T,p)$	Enthalpy of combustion at temperature T and pressure p.
B	Second virial coefficient in volumetric units
B^*	Second virial coefficient in pressure units
$B(T)$ or $B^*(T)$	Second virial coefficient, indicating that it is a function of temperature
$B(i)$	Second virial coefficient of substance i
$B(1,i)$	Virial coefficient for binary interaction of methane (1) with another substance (i)
B(mixture)	The virial coefficient of a mixture Note: For methane (1) - mixed with one other component (i): $B(\text{mixture}) = [x(1)]^2B(1) + 2x(1)x(i)B(1,i) + [x(i)]^2B(i)$

$x(i)$	mole fraction of component i
$w(i)$	mass fraction of component i
$M(i)$	relative molecular mass of substance i
V_m°	ideal gas molar volume
R	the gas constant
C_p°	standard heat capacity at constant pressure
ΔC_p°	ΣC_p°(products) - ΣC_p°(reactants)
Z	compression factor, pV/RT (commonly called compressibility factor)

Appendix 3. Definitions of terms as used in this document.

A3.1 Terms relating to quantities and concepts.

A3.1.1 Atomic weight - the atomic weight is the dimensionless relative mass of an atom or of a mole of atoms of normal isotopic composition based on a scale in which the isotope ^{12}C has a relative mass of 12. Preferred name is relative atomic mass, q.v.

A3.1.2 Compression factor - The compression factor (symbol Z) is the ratio

$$Z = pV_m/RT$$

For an ideal gas $Z = 1$, but for real gases, Z differs from unity by amounts that are small but significant at reference conditions.

A3.1.3 Dry gas - Dry gas is a gaseous substance or mixture containing little or no water vapor.

A3.1.4 Enthalpy - Enthalpy (symbol H) is a thermodynamic property of a material, representing the internal energy U plus the pV work associated with its volume and pressure.

$$H = U + pV.$$

Enthalpy is often called heat content. Enthalpy, per se, is not measurable but enthalpy differences are.

A3.1.5 Enthalpy of combustion - The enthalpy change occurring when a combustion reaction occurs with all reactants and products reduced to the same specified temperature. It is often called heat of combustion and has a negative value for all fuels. The negative of the enthalpy of combustion of a fuel is often called calorific value, heating value, net calorific value (q.v.), or total calorific value (q.v.). Standard enthalpy of combustion is the enthalpy of combustion calculated for the condition when all substances are in their thermodynamic standard states (see standard state). For gaseous substances this state is the ideal gaseous state.

A3.1.6 Enthalpy of formation - The enthalpy of formation is the enthalpy change occurring when a substance is formed from the elements; the elements and the substance being at the same specified temperature. The standard enthalpy of formation is the enthalpy of formation when the substance and the elements are in their thermodynamic standard states. For gaseous elements this state is the ideal gaseous state.

A3.1.7 Equation of state - The equation of state of a substance is the mathematical expression expressing the relationship among the amount of substance n, the volume it occupies V, the thermodynamic T and the pressure p. For an ideal gas. $V/n = RT/p$, where R is the gas constant. See also virial coefficient.

A3.1.8 Gas constant - The gas constant (symbol R) is the proportionality factor relating the thermodynamic temperature T to the pV work associated with the pressure p and the volume per mole V_m=(V/n) of an ideal gas.

A3.1.9 Heat capacity - The heat capacity at constant pressure, C_p, of a substance is an extensive property that is the rate of increase of enthalpy of the substance with temperature; $C_p = (\partial H/\partial T)_p$. If the amount of substance is one mole, then it is more properly termed the molar heat capacity, an intensive property.

A3.1.10 Ideal gas - An ideal gas is a hypothetical gas that conforms exactly to the ideal gas law:

$$pV_m = RT$$

in which p is the pressure, V_m is the molar volume, T is the thermodynamic temperature, and R is the gas constant.

A3.1.11 International Practical Temperature Scale - The International Practical Temperature Scale (IPTS) is the closest feasible approximation to the thermodynamic temperature scale as realized by a series of defined fixed temperatures and interpolation formulas and agreed upon at intervals by the International Bureau of Weights and Measures (BIPM) with advice from the Consultative Committee on Thermometry (CCT). The scale is changed slightly from time to time, and the date of adoption of a new set of values is specified; e.g., IPTS-68 is the International Practical Temperature Scale of 1968. For very precise work the temperature T may also be identified by the year of the IPTS; thus T_{68} is a temperature measured on the scale IPTS-68.

A3.1.12 Molar mass - The molar mass of a substance is the mass of a mole of the substance of specified formula, based on a scale on which one mole of the isotope ^{12}C has a mass of 12 grams (exactly).

A3.1.13 Molecular weight - A dimensionless relative mass of a molecule (or of a mole of molecules in which all the atoms have their normal isotopic compositions) based on a scale in which the isotope ^{12}C has a relative mass of 12. Preferred name is relative molar mass, q.v.

A3.1.14 Net calorific value - The net calorific value (net, lower or inferior heating value) is the heat evolved by the complete combustion, at constant pressure, of a unit amount of gas with air, when the gas, air, and products of combustion all are at a specified reference temperature and pressure, and all the water formed by the combustion reaction remains in the the vapor state. See notes under total calorific value.

A3.1.15 Real gas - "Real gas" is a descriptive term identifying actual gas behavior as contrasted with the hypothetical ideal gas (q.v.) The actual volume occupied by a given amount of a real gas at a given temperature deviates from that calculated by the ideal gas law by amounts that are small but significant at reference conditions.

A3.1.16 Relative atomic mass - The relative atomic mass is the dimensionless relative mass of an atom (or of a mole of atoms of normal isotopic composition) based on a scale in which the isotope ^{12}C has a relative atomic mass of 12. This term is preferred to "atomic weight", but is identical in meaning.

A3.1.17 Relative molecular mass - The relative molecular mass, formerly called "molecular weight", is the ratio of the average mass per formula unit of a substance to 1/12 of the mass of an atom of nuclide ^{12}C.

A3.1.18 Reference (standard) conditions - Reference (standard) conditions are conditions of temperature, pressure, and degree of saturation with water to which measurements of gas volumes or properties are reduced to allow comparability among measurements made under possibly different conditions. See table 2.

A3.1.19 Specific heat capacity - The specific heat capacity of a material is the heat capacity (q.v.) per unit mass of material. The term "specific heat" is ambiguous and incomplete and is now deprecated.

A3.1.20 Standard state - The standard thermodynamic properties for a gaseous substance, whether pure or in a gaseous mixture, apply to the pure substance at the standard state pressure and in a hypothetical state in which it exhibits ideal gas behavior. These conditions of temperature, pressure and ideal behavior define the standard state. When a property of a gas refers to the gas in its standard state it is designated with a superscript °, i.e. H° is the enthalpy of a substance in the standard state.

A3.1.21 Total calorific value - The total calorific value (total, superior or gross heating value) of a gas is the heat evolved by the complete combustion, at a constant pressure, of a unit amount of gas with air, when the gas, air and products of combustion all are at a specified refer temperature and pressure, and all the water formed by the combustion reaction is condensed to the liquid state.

Note 1. The heat evolved is the negative of the enthalpy change for the specified process. The heat may be measured in joules or British thermal units.

Note 2. The amount of a gas may be measured as an amount of substance (moles), as a mass (kilograms or pounds), or as a volume measured under standard reference conditions (cubic meters or cubic feet).

Note 3. See table 2 for reference conditions that are in use or have been used.

Note 4. The gross heating value of a gas is greater than the gross heating value of the liquid of the same composition by the enthalpy of vaporization of the liquid.

Note 5. The gross heating value of a gas is greater than its net heating value by the enthalpy of vaporization of the water formed in the combustion.

A3.1.22 Vapor pressure - The vapor pressure of a substance is the pressure in the vapor of a substance when equilibrium exists between the vapor and a condensed phase of the substance.

A3.1.23 Virial coefficient - The virial coefficients are the constants B, C, D or B^*, C^*, D^*, in the virial equation of state which describes the behavior of a real gas and which may take the form:

$$pV_m/RT = 1 + B(T)/V + C(T)/V^2 + D(T)/V^3 + \ldots..$$

or the form:

$$pV/RT = 1 + B^*(T)\cdot p + C^*(T)\cdot p^2 + \ldots$$

The virial coefficients are functions of temperature T. $B(T)$ or $B^*(T)$ is the second virial coefficient; $C(T)$ or $C^*(T)$ is the third virial coefficient, and so on. In this document no terms higher than B are used. See Section 10 and Appendix 9.

A3.1.24 Volume under standard conditions - The volume under standard conditions, symbol V_{std}, is the volume occupied by a measured or specified amount of gas when under standard conditions of temperature, pressure and degree of saturation with water. (cf. standard cubic foot). This is a volume and as such has the unit cubic metre or cubic foot.

A3.1.25 Water-saturated gas - A gaseous mixture in which water vapor is present at the saturation vapor pressure for the temperature and other conditions of measurement.

A3.2 Terms that are units of measurement.

A3.2.1 Atmosphere - The atmosphere (symbol atm) is an obsolescent unit of pressure, equivalent in various usages to 760 mmHg, 30 inHg, and 14.7 psia (more or less). It has been most recently defined as 101.325 kPa (exactly).

A3.2.2 British thermal unit (symbol Btu) - The British thermal unit is a customary (U.S. or British) unit for the measurement of amounts of energy, particularly when observed as heat. It was initially defined in terms of the specific heat capacity of water as the amount of heat needed to raise the temperature of one pound (mass) of water one degree Fahrenheit, but is now by consensus usually defined in terms of the joule. The International Tables British thermal unit (symbol Btu_{IT}) is used in this document and is defined by the relationship 1.8 Btu lb^{-1} = 4.1868 J g^{-1}. This gives it the exact value, 1 Btu_{IT} = 1055.05585262 J, which may be rounded to 1055.056 J. Gas industry measurements until a few years ago were often made using a British thermal unit defined as the heat needed to raise the temperature of one pound of water from 58.5 to 59.5 °F (the Btu_{59F}). The value depends upon the value used for the specific heat capacity of water, but differs from the Btu_{IT} by about 0.252 J, a significant amount, See ref. [1] in the General List. This unit is now deprecated. For each defined Btu there is a corresponding calorie. They are related by 1 Btu/lb·°F = 1 cal/g·°C.

A3.2.3 Joule - The joule is the work done when the point of application of a force of one newton is displaced a distance of one metre in the direction of the force. It is also the value of the pV term of a gas occupying a volume V = 1 m^3 at a pressure p = 1 Pa.

A3.2.4 Newton - The newton is that force which, when applied to a body having a mass of one kilogram gives it an acceleration of one metre per second per second.

A3.2.5 Pascal - the pascal is the pressure produced by a force of one newton on an area of one square metre.

A3.2.6 Standard cubic foot of gas - The standard cubic foot (symbol scf) of a gas is the quantity of any gas that, at standard temperature and under standard pressure, will fill a space of one cubic foot when in equilibrium with water vapor. See Section 6 for standard conditions. Note that this is a unit of amount of substance. Cf. "volume under standard conditions", which is a preferred term for describing volumetric measurements of gas.

A3.2.7 Torr - The torr is an obsolescent unit of pressure defined as 1/760 atm. By this definition it is essentially equal to 1 mmHg, but the dependence on the value for the density of mercury has been removed.

Appendix 4. Units of measurement and conversion factors

Table A4. Measurement quantities defined exactly in terms of SI units

Name	Symbol	Equivalent
	Length	
inch	in	0.0254 m
foot	ft	0.3048 m
yard	yd	0.9144 m
	Mass	
ounce (avoir)	oz	0.028 349 523 125 kg
pound (avoir)	lb	0.453 592 37 kg
	Area	
square inch	in^2	6.451 6 cm^2
square foot	ft^2	9.290 304 dm^2
square yard	yd^2	0.836 127 36 m^2
	Volume	
cubic inch	in^3	16.387 06 cm^3
cubic foot	ft^3	0.028 316 847 m^3
cubic yard	yd^3	0.764 554 9 m^3
litre	L	0.001 m^3
gallon (U.S. liquid)	gal	0.003 785 412 m^3
	Pressure	
atmosphere (760 Torr, 760 mmHg, 0 °C)	atm	101.325 kPa
kilogram force per square metre		9.806 650 Pa
torr (101325/760)Pa (1 mmHg, 0 °C)	Torr	133.322 . . . Pa (Note a)
pound force per square inch	psi	6894.757 . . . Pa (Note a)
($9.80665 \times 0.45359237/6.4516 \times 10^{-4}$) Pa		

Table A4. (Cont'd)

Name	Symbol	Equivalent
millemetre of mercury (see torr)	mmHg	133.222 . . . Pa (Note a)
bar	bar	100.000 kPa
	Temperature	
degree Celsius	°C	K
degree Fahrenheit	°F	5/9 K
temperature, Celsius	t/°C	T/K - 273.15
temperature, Fahrenheit	t/°F	1.8t/°C + 32
temperature, Rankine	T/°R	1.8 T/K
		1.8t °C + 491.67
		t °F + 459.67
	Energy	
calorie (international tables	cal_{IT}	4.1868 J
calorie (thermochemical)	cal_{th}	4.184 J
British thermal unit (international tables)	Btu_{IT}	1.055 055 852 62 kJ (exactly) (Note b)

Note a: While the Torr and the psi are defined as exact ratios, the ratios are continuing fractions. See discussion of mmHg at Table 2 and Appendix 5b.

Note b: The Btu_{IT} is defined by the relationship:

$$kJ/Btu_{IT} = (J/cal_{IT})(K/°F)(kg/lb)$$

$$= (4.1868)(1/1.8)(0.45359237)$$

Appendix 5. Discussion of physical constants

Appendix 5a. Relative atomic and molecular masses

Table A5a gives a listing of six differing sets of relative atomic masses (atomic weights) for the elements C, H, O, N that have been recommended since 1941 plus the set used in the International Critical Tables. They are coded A to G in order of increasing age. The set selected for this document is Set A, which was chosen for two reasons: (1) It is the current recommendation of the IUPAC Commission on Atomic Weights and Isotopic Abundances [1] and represents the best estimate based on modern research of the atomic masses. (2) It is only slightly different than the set that has been recommended for ten years [2]. The only noticeable difference is the value for hydrogen which, at five significant figures, rounds to the value given in Set B.

Lines A and A' in Table A5a are both part of the current recommendation. The first line (A) gives values to the decimal place in which there is some uncertainty. (The uncertainties are given in Table A5c). Variation in natural terrestrial samples is the principal cause of uncertainty for the elements of interest here. The five-significant-figure set coded A' has values that are less accurate, but are more likely to remain constant for a decade, even with continued research into the matter.

Table A5b gives for each set of atomic masses the relative molecular masses of CH_4, CH_2 and CH, which represent respectively the maximum H/C ratio the limiting H/C ratio for homologous series, and the minimum H/C ratio encountered in the common low molecular mass hydrocarbons. Also given are the relative molecular masses calculated for H_2O and CO_2 using each set.

The uncertainties introduced into the calculations by the variability with time of the recommended atomic masses are indicated in the footnote to Table A5b. This also shows the level of error due to atomic mass changes that can be introduced when measurements made at different times are compared without adjustment for the changes in molar masses.

An examination of compilations of thermodynamic data for hydrocarbons has shown that sets B, C, D, F and G have been used. There has been no clear preference. Nor have the recent recommendations (in the 1970's) been used often. Some examples are given in Appendix 7 where sources of data are presented.

The procedure used in this document to calculate relative molecular masses is to use Set A and then round the value of the molecular mass to the decimal place in which the accumulated error appears. This procedure is displayed in Table A5c. The uncertainties in the atomic masses used in that table are those recommended by the IUPAC Commission. Because those uncertainties allow for samples from many sources, the resulting errors may be considered large for fossil fuels. Nevertheless, the uncertainty in the relative atomic mass of carbon make it appropriate to round molecular masses of the hydrocarbons of interest to three decimal places.

Table A5. Atomic masses

Table A5a. Recent sets of relative atomic masses of the chemical elements and their period of recommendation by the International Union of Pure and Applied Chemistry (IUPAC)

	C	H	O	N	Year first recommended
A	12.011	1.00794	15.9994	14.0067	1981 [1]
A'[(a)]	12.011	1.0079	15.999	14.007	1981 [1]
B	12.011	1.0079	15.9994	14.0067	1971 [2]
C	12.011	1.0080	15.9994	14.0067	1969 [3a]
D	12.01115	1.00797	15.9994	14.0067	1961 [3b]
E	12.011	1.0080	<u>16</u>[(b)]	14.008	1953
F	12.010	1.0080	<u>16</u>	14.008	1941
G	12.000	1.0077	<u>16</u>	14.008	1923[(c)]

(a) The A' line has the five-significant-figures set given by the IUPAC Commission on Atomic Weights. These are values rounded from Set A. Set A' also includes Ar, 39.948; He, 4.0026; S, 32.06. The certainty of the value for sulfur is limited to four significant figures by the range of isotopic compositions in normal terrestrial materials.

(b) The relative atomic mass of oxygen in set E and earlier sets is an integral value by definition.

(c) Prepared by G. P. Baxter for the International Critical Tables. The first international recommendation (1931) gave C = 12.00 and H = 1.0078. There were several changes during the 1930's.

Table A5b. Relative molecular masses of some important molecules as formally calculated from different sets of relative atomic masses (rounded to four decimal places). See Table 1 for recommended values

SET	CH_4	CH_2	CH	H_2O	CO_2
A	16.0427	14.0269	13.0189	18.0153	44.0098
B	16.0426	14.0268	13.0189	18.0152	44.0098
C	16.0430	14.0270	13.0190	18.0154	44.0098
D	16.0430	14.0271	13.0191	18.0153	44.0099
E	16.0430	14.0270	13.0190	18.0160	44.011
F	16.0420	14.0260	13.0180	18.0160	44.010
G	16.0308	14.0154	13.0077	18.0154	44.00

Maximum relative differences in molecular masses from sets A through F. The letters in parenthesis identify the sets giving the maximum deviation listed.

CH_4, $4.4 \cdot 10^{-5}$(D/F); CH_2, $7.8 \cdot 10^{-5}$(D/F); CH, $8.6 \cdot 10^{-5}$(D/F); H_2O, $6.6 \cdot 10^{-5}$ (E,F/B); CO_2, $4.4 \cdot 10^{-5}$(E/A).

Table A5c. Assignment of uncertainties in relative atomic and molecular masses for the 1981 set recommended by the IUPAC Commission on Atomic Weights and Isotopic Abundances

Assign *s* (the estimated uncertainty of values in Table 1) as follows:

Element	Relative atomic mass	Uncertainty $s \times 10^4$
	atomic weight unit	
Ar	39.948	1.
C	12.011	10.
H	1.00794	0.7
He	4.00260	0.1
O	15.9994	3.
N	14.0067	1.
S	32.06	100.

Table A5c. (continued)

Calculation of absolute and relative errors in relative molecular masses using data in Table A5c.

Molecule	Atoms and weights	Uncertainties[a] Additive 10^4 s	Quadrature 10^8 s^2	Quadrature 10^4 s
CH_4	C 12.011	10	100	
	H 4 x 1.00794	4 x 0.7	8	
	16.04274	12	$(108)^{1/2}$	= 10.
Rounded value[b]: 16.043				
Relative uncertainty: divisor 16.04		0.7		0.6
CH	C 12.011	10	100	
	H 1.00794	0.7	0.5	
	13.01894	11.	$(100)^{1/2}$	= 10.
Rounded value: 13.019				
Relative uncertainty: divisor 13.02		0.3		0.24
CO_2	C 12.011	10	100	
	O_2 31.9988	6	36	
	44.0098	16	$(130)^{1/2}$	= 12
Rounded value: 44.010				
Relative uncertainty: divisor 44.01		0.2		0.15
H_2O	H 2 x 1.00794	2 x 0.7	2	
	O 15.9994	3	9	
	18.01528	4.4	$11^{1/2}$	= 3.3
Rounded value: 18.0153				
Relative uncertainty: divisor 18.02		0.2		0.2

[a]The uncertainties by quadrature (square root of sum of squares) are recommended. See Appendix 10 on propagation of errors.

[b]The rounded values also appear in Table I. Other values there were determined by similar procedures.

References for Appendix 5a.

[1] IUPAC Commission on Atomic Weights and Isotopic Abundances; "Atomic weights of the elements 1981"; Pure and Applied Chemistry (1982) in press.

[2] IUPAC Commission on Atomic Weights; "Atomic weights of the elements 1971"; Pure and Applied Chem. (1972), 30, 637-649.

[3] a. IUPAC Commission on Atomic Weights, "Atomic weights of the elements"; Pure and Applied Chemistry (1970), 21, 91-108; and J. Am. Chem. Soc. (1971), 93, 2579. b. Cameron, A. E.; Wichers, E. J.; "Report of the International Commission on Atomic Weights (1961"; J. Am. Chem. Soc. (1962), 84, 4175.

Appendix 5b

The density of mercury, the standard acceleration of gravity, and the significance of the reference pressure 760 mmHg.

The density of mercury serves three slightly different purposes: (1) to convert barometric and manometric pressure measurements using a mercury column to a uniform basis in terms of the standard millimetre of mercury or standard inch of mercury as a unit of pressure; (2) to convert old data reported in standard millimetres or inches of mercury using standard barometric tables to a pressure unit consistent with the mechanical units of pressure, SI units; and (3) to convert accurate pressure measurements made using a mercury column as a sensor directly to pressure in the SI units. It should be recognized that the actual density of mercury is a function not only of temperature but also of pressure and isotopic composition, and furthermore that the experimental determination of the density as a function of these variables is subject to experimental uncertainties that change as improved procedures are introduced. We cannot go into the details of these factors and their treatment over the years, and shall give only a sketch of the principal points related to the usage of the millimetre of mercury as a unit of pressure.

The conclusion that has been drawn from this historical survey is that the standard atmosphere and 760 mmHg are identical today. Except, perhaps, for measurements of the highest precision, the two units have been the same for eighty years.

1. The General Conference on Weights and Measures, CGPM, in 1901 (Resolution 3) adopted the value 980.665 cm s^{-2} for the standard (normal) acceleration of gravity [1]*. This was confirmed in 1913 [2, p. 16].

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*References cited here are listed at the end of Appendix 5b.

2. In 1913, Chappuis [3] presented selected values for the density and coefficient of expansion of mercury and gave $\rho_{Hg}(t = 0\ °C) = 13.59515$ g cm^{-3}, under normal pressure, using the density of water at 4 °C = 0.999973 g cm^{-3}. He cites earlier work (Chappuis (1907), [4]) for the coefficient of expansion and cites Marek (1883), [5] (d_0 = 13.5956) and Thiesen and Scheel (1897), [6], (d_0 = 13.59545) for the density of mercury at 0 °C relative to that of water at 4 °C. He took the average of these and chose d_0 = 13.59552 from which he obtained the value listed above for the absolute density of mercury. The uncertainty in the value given is ± 0.00008 based only on the range of values from which it was derived.

3. In 1917 Leduc [7] used for standard conditions in determining the standard density of air: p = 76 cm Hg, g = 980.665 cm s^{-2}, and ρ_{Hg}(at t = 0 °C) = 13.5951 g cm^{-3}, for which, however, he gave no citation of source.

4. The Smithsonian Meteorological Tables (Fourth Revised Edition, 1918) [8] introduced new tables for converting millimetres of mercury to millibars using the standard acceleration of gravity adopted by the CGPM in 1901 (980.665 cm s^{-2}), and the density of mercury ρ_{Hg}(at 0 °C) = 13.5951 g cm^{-3}, taken from Chappuis [3] and Leduc [7]. These tables were widely used in the United States for the correction of manometric and barometric measurements using mercury as an indicator to pressures.

5. N. E. Dorsey (1926), [9] for the International Critical Tables, defined the normal atmosphere as the pressure exerted by a vertical column of liquid 76 cm long, density 13.5951 g cm^{-3}, acceleration of gravity being 980.665 cm s^{-2}. Incidentally, the British atmosphere is stated to be based on 30 inches (76.2 cm) rather than 76 cm.

6. In 1926 Kimball [10], for the International Critical Tables section on barometry and manometry, gave the standard density of mercury as 13.5951 g cm^{-3}, and the standard acceleration of gravity of 980.665 cm s^{-2} without reference, but his temperature corrections are referred to the International Meteorological Tables [11]. (We have not found those numbers in the IMT, they may have been derived by Kimball).

7. In 1927 the Bureau of Standards, the National Physical Laboratory and the Physikalische Technische Reichsanstalt submitted a text of a proposed international temperature scale in which the standard (normale) atmospheric pressure is defined as the pressure exerted by a column 760 mm in height of mercury having an average density of 13.595 g cm^{-3} under an acceleration of gravity equal to 980.665 cm s^{-2}; equivalent to 1 013 250 dynes cm^{-2} [CGPM 1927, ref. 12]. No source is given for the numbers, but they were modified and reiterated in 1933 [13] with a corrected text in which the density of mercury is changed to 13.5951 g cm^{-3}. The number thus conforms to the value given by the Smithsonian Meteorological Tables. The numbers are related by the relationship:

$$1\ 013\ 250/(980.665 \cdot 76) = 13.595098$$

or by:

$$12.5951 \cdot 76 \cdot 980.665 = 1\ 013\ 250.14$$

Thus it is apparent that a value for the standard atmospheric pressure had been chosen to be in close accord with a standard height (76 cm) of a column of mercury of average density equal to the best known value at the time, and under the standard acceleration of gravity. It will be noted that the specified average density is slightly less than the value at normal pressure given by Chappuis in 1913 [3]. This is consistent with the fact that the average pressure on the mercury in a barometer is only 1/2 the external pressure and thus the average density should be less than that given by Chappuis. The deviation should be about 3×10^{-5} g cm^{-3} which would reduce Chappuis' value to 13.59512 with an uncertainty of 0.00008. The value rounded to 13.5951 thus contains the last significant figure.

8. In 1948 the CGPM presented the international temperature scale of 1948 which reiterated the previous standard pressure in all details [14, pg. 93]. However, a change of emphasis occurred. The standard pressure [14, pg. 90] is defined as 1 013 250 dynes cm^{-2} and the mercury scale is related to it. It adds that except for work of the highest precision one can accept that the mercury of commerce has the specified average density 13.5951 g cm^{-3} in the column of 760 mm.

9. The CGPM, in 1954 considered the definition of the standard atmosphere in 1948 might be construed as applying only to precision thermometry [15]. It, therefore, adopted a resolution (Resolution 4) defining one standard (normale) atmosphere as 1 013 250 dynes cm^{-2} or 101 325 newtons per square metre, thus validating definitively the standard value to be used, and removing any ambiguity about the calculations given in paragraph 7.

10. In 1957 Cook and Stone [16] reported some measurements of the density of mercury at 20 °C and reported:

$$\rho_{Hg}(20\ ^{\circ}\mathrm{C}) = 13.545\ 8924\ \mathrm{g\ cm^{-3}}$$

which reduces at 0 °C to 13.595 0889 g cm^{-3}. Cook (1961, ref. 17) extended these measurements and reported a summary value including both sets of ρ_{Hg}(at 20 °C, 1 atm) = 13.545 884 g cm^{-3} which, reduced to 0 °C, becomes:

$$\rho_{Hg}(0\ °C,\ 1\ atm) = 13.595\ 080\ g\ cm^{-3}\quad ,$$

with a standard deviation of 0.2 x 10^{-6} (0.2 ppm). These densities at t = 0 °C round to 13.5951 g cm^{-3}. Thus the value used traditionally for barometry and manometry is accurate in the sixth figure.

11. Brombacher, Johnson, and Cross (1960, ref. 18) for the NBS monograph on mercury barometers and manometers used the value ρ_{Hg}(0 °C) = 13.5951 g cm^{-3}, the standard atmosphere, 1013.250 mbar, and the standard acceleration of gravity 980.665 cm s^{-2}.

12. In 1960, the eleventh General Conference on Weights and Measures adopted the International Practical Temperature Scale of 1948 amended 1960 [19, pg. 63]. In the amended text [19, p. 127] the statements are made that in practice pressures are determined by means of a column of mercury and that one can assume that the density at 20 °C of pure mercury is 13 545.87 kg m^{-3} as an average in a column of mercury that balances 1 atmosphere. They also recommended the use of the Potsdam system for determination of local gravity for realization of the standard atmosphere.

13. In 1964 Bigg [20] reviewed the density of mercury and used the data of Cook [17] and the thermal expansion formula of Beattie et al [21] which is the same as was used by Cook, to calculate a table of densities of mercury as a function of temperature at P = 1 atm. He tabulated ρ_{Hg}(20 °C) = 13.545 88 g cm^{-3} and ρ_{Hg}(0 °C) = 13.59508 g cm^{-3} which are the rounded values of Cook.

14. Bonhoure and Terrien [1968, ref. 22] working at the International Bureau of Weights and Measures, BIPM, used for the density of their mercury column the density at mid height, $\rho(\text{mean})^*$, and used the formula:

$$\rho(\text{mean}) = \rho_o/[1 - \alpha_{Hg}(t_{Hg} - 20\ °C)][1 - \beta_{Hg}(p/2 - p_N)]$$

for which ρ_o, the density of mercury at 20 °C = 13.545 892 g cm^{-3} obtained from Cook and Stone [13], $\alpha_{Hg} = 181.1 \times 10^{-6}\ K^{-1}$, $\beta_{Hg} = 39 \times 10^{-12}\ m^2\ N^{-1}$ and $p_N = 101\ 325\ N\ m^{-2}$. The density given at 20 °C can be derived from the formula and data of Bonhoure and Terrien. The term $-\beta(p/2 - p_n)$ becomes $+\ 1.975 \times 10^{-6}$, and this leads to $\rho_{Hg}(20\ °C, \text{mean}) = 13545.8652\ kg\ m^{-3}$. If the more recent work of Cook [14] is used for ρ_o, $\rho_{Hg}(20\ °C) = 13545.884\ kg\ cm^{-3}$, then $\rho_{Hg}(20\ °C, \text{mean}) = 13545.857\ kg\ m^{-3}$.

15. In 1968 the 13th CGPM adopted the International Practical Temperature Scale of 1968 ([23], resolution 8, p. 62, p. 105; full text, pp. A1-A24). The formula for calculating the density of mercury as a function of temperature and pressure is given as :

$$\rho(t_{68},\text{mean}) = \rho(20\ °C,\ p_o)/[1 + A(t_{68} - 20\ °C) + B(t_{68} - 20\ °C)^2] \times [1 - x(p/2 - p_o)]$$

where $A = 18115 \times 10^{-8}\ °C^{-1}$; $B = 0.8 \times 10^{-8}\ °C^{-2}$, $x = 4 \times 10^{-11}\ N^{-1}\ m^2$, and $\rho(20\ °C,\ p_o) = 13545.87\ kg\ m^{-3}$ for pure mercury when $p_o = 101\ 325\ N\ m^{-2}$. The term $-x(p/2 - p_o)$ has the value $+\ 2.0265 \times 10^{-6}$. The value of $\rho_{Hg}(20\ °C, \text{mean}) = 13545.842\ kg\ m^{-3}$.

The temperature correction to $t = 0$ °C is:

$$\rho(20\ °C)/\rho(0\ °C) = 1 - 20 \times 18\ 115 \times 10^{-8} + 400 \times 0.8 \times 10^{-8} =$$

$$1 - 0.00362300 + 0.000003_2 = 0.9963802$$

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*We use the term ρ(mean) in all cases where authors have referred to pressures at mid height, at p/2 or average densities.

$\rho_{Hg}(0\ °C, \text{mean}) = 13595.053\ kg\ m^{-3}$. The value resulting from a similar calculation but not using the CGPM (1968) formula was found by Armstrong [24] to be $\rho_{Hg}(20\ °C, \text{mean}) = 13595.052\ kg\ m^{-3}$ in good agreement.

16. Brown and Lane [25] reviewed the density of mercury in 1976. They cited the formula and constants as given by CGPM in 1968 [23] and presented a table for $\rho_{Hg}(t_{68}, p_0)$ derived in the same way as that of Bigg [20] except converted to IPTS-1968. They used $p_0 = 101.325$ kPa and tabulated $\rho_{Hg}(0\ °C, p_0) = 13595.08\ kg\ m^{-3}$ in exact agreement with the value calculated by Cook [17].

As a result of this survey, it is quite clear that for precise measurements of pressure using a mercury column (purpose 3 above) the accurate determination of density by Cook [17] and interpolation formulas such as are given by Brown and Lane [25] should be used. However, it is also clear that the standard millimetre of mercury used in establishing the relationship between the standard atmosphere specified as 760 mm Hg and the standard atmosphere as 101.325 kPa is not based on the recent measurements of Cook but is based on much earlier measurements. The value used for the density of mercury, $\rho_{Hg}(0\ °C, \text{average}) = 13.5951\ g\ cm^{-3}$, was given official standing by CGPM in 1927 (as corrected in 1933) and confirmed in 1948. This density was derived by Chappuis in 1913 from earlier measurements and shortened to the present last significant figure (six figures) by Leduc in 1917. It was adopted by such internationally used compilations as the International Critical Tables and the Smithsonian

Meteorological Tables, and finally placed in the status of a defined value by CGPM.

The exact process has not been discovered by which the decision was made that the standard atmosphere should be 101.325 kPa (101 3250 dynes cm^{-2}) exactly, rather than a column of height 760 mm of mercury of density 13.5951 g cm^{-3} in a standard gravity of 980.665 cm s^{-2}.

It is clear however, on the basis of the CGPM decisions in 1933 and 1948 that the selected pressure was, within the limits of accuracy of the measurements, identical on the two bases.

We believe the relationships given in paragraph 7, above, constitute a definition of the unit, mmHg, which is most applicable to pressure measurements made during the long period from about 1917 to 1957, that there is no point in refining further an obsolescent unit and that the accuracy of the quantities measured does not warrant defining the mean ρ_{Hg}(0 °C), to greater than six figures for the purpose of identifying the pressure reference condition.

The value chosen for this document is therefore:

$$\rho_{Hg}(0\ ^\circ\mathrm{C},\ \mathrm{mean}) = 13595.1\ \mathrm{kg\ m^{-3}}$$

Within the limits of measurement the unit of pressure, mmHg, is identical to the Torr, i.e.

$$1\ \mathrm{mmHg} = 1\ \mathrm{Torr} \equiv \frac{101\ 325\ \mathrm{Pa}}{760} = 133.322\ \mathrm{Pa}\quad ,$$

These correspondences are included in the ASTM standard for Metric Practice [26]. On this basis a reference pressure of 760 mmHg is identical to 101.325 kPa.

References to Appendix 5b

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Appendix 6. Discussion of reference conditions

The values of pressure, temperature, state of gas, and water content to be used for defining the reference conditions of measurement of natural gas are listed in table 2. Various standardizing bodies have selected different values or conditions of these parameters for "base conditions" or reference conditions. The actual values used in the measurement of the properties of a gas are extremely important in custody transfer as well as in calculations of performance if comparability of the heating value of the gas is to be realized. This is particularly true for volumetric measurement of gas because the volume occupied by a given quantity of the gas is strongly dependent on them. To a lesser extent, though still significantly, the heating value of a given mass of gas is dependent on these parameters. The values for these parameters that have been recommended by various groups are discussed below.

Temperature. For many years in the United States a reference temperature of 60 °F (15 5/9 °C, 288.7055 ... K, rounded to 288.71 K) has been used both in the natural gas industry, and in petroleum products industries as the temperature to which volumetric measurements and measurements of properties should be referred, whereas European practice has been to use 15 °C [9a]*. In recent years in an attempt to bring greater conformity to U.S. and European measurement practices, U.S. practice has been moving to the adoption of 15 °C (59 °F or 288.15 K) as a reference temperature. See, for instance [1] or [9b]. ASTM Committee D-3 on Gaseous Fuels has recently adopted 15 °C as the reference temperature for metric measurement of natural gas samples [9b] as has the American Gas Association; and the American Petroleum Institute appears also to be adopting 15 °C for gas measurements [10].

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*References cited in this appendix are in the General List.

On the other hand, for many years scientifically oriented measurements universally have often been referred either to 25 °C (298.15 K) or 0 °C (273.15 K) as a standard temperature [8]. The former temperature is cited in many compilations of the properties of hydrocarbons. See for examples Table A7e in Appendix 7. T = 273.15 K is used in Japan as the reference temperature. Because there is widespread use of each of these four temperatures information is given in this handbook for converting measurements from one of these temperatures to another. However, 15 °C (288.15 K) and 60 °F (288.7055 ... K) are the reference temperatures selected for presentation of the tables of heating values measured on a volumetric basis.

Pressure. The situation with respect to reference pressure is much the same as with respect to temperature. European practice has been to use 101.325 kPa (1 atm). Early gas industry practice in the United States emphasized a pressure base of 30 inHg (762 Torr, 101.5913 kPa) which converts to 14.7345+ psia; and was often rounded to 14.73 psia (101.559.77 kPa which is rounded to 101.560 kPa). However usage of other pressure bases has been widespread.

The pressure 14.73 psia was adopted by ANSI in 1969 (ANSI Z 132.1 - 1969) [10] apparently without reference to existing standards which defined the base pressure as 30 inHg, a round number that can be presumed intended to be exact: ASTM D 1071-55; USA Standard Z 77.5 - 1963 (Later American National Standard Z 77.5 - 1973) and ASTM D 900-55; USA Standard Z 68.1 - 1956 (later American National Standard Z 68.1 - 1973). It is unclear whether 14.73 psia was intended to be equivalent to 30 inHg or whether it was intended to be exact. Unfortunately the difference is significant in tabulated values of enthalpies of combustion of gaseous hydrocarbon compounds on a volumetric basis. The difference is, however, less than other uncertainties in the measurement of total heating value. Because ASTM has followed the lead of ANSI in the use of this number (see ASTM D 1071-78a, ref. 9b) we use the value 14.73 pisa as exact in making the calculations, and not as a shorthand notation for 30 inHg.

In scientific work a slightly different pressure, usually called the standard atmosphere (1 atm = 101.325 kPa by definition [2,5]) has been used for many years. This pressure has been recently adopted in ASTM standards for measurement of gaseous volumes in metric units and by the American Gas Association and is apparently being adopted by the American Petroleum Institute [10]. This pressure has been used also as the standard state pressure for reporting thermodynamic quantities. However, recent action by IUPAC Commission on Thermodynamics [3] recommends that a new pressure, 100.000 kPa (=1 bar), be adopted as the standard pressure to which the thermodynamic standard state would apply. While widespread usage of this new reference pressure may not occur until some time in the future, notice is taken of it in this document.

Information is given to allow calculations to be made for each of these three reference pressures. However, for consistency with gas industry measurement practice the tables are given for the reference pressure of 101.325 and 101.560 kPa.

<u>Gas ideality</u>. The use of real gas properties is universal in practical measurements in the gas industry. However, the properties of real gas mixtures are functions of the composition. As a result of the fact that tabulation of the properties of all real gas mixtures is impossible, and because the components of natural gas (other than CH_4) are generally present as a small fraction of the total gas it is more useful to emphasize ideal gas properties for the pure gases and to utilize the virial coefficients and compositions for calculation of the properties of mixtures on an ad hoc basis.

Water content. Natural gas in production, transmission and distribution usually has a relatively low water content. Hence, for most purposes the dry gas is a better reference state than the water-saturated gas. However, for determination of heating value by the continuous flow recording combustion calorimeter, the measurement devices require the gas to be water-saturated before combustion. This is because the wet test meters used for metering the amount of gas burned are water-filled, and because the entering gases must be water-saturated in order to assure that all the water formed is condensed to the liquid state in the calorimeter in order to determine the gross heating value. Thus for determination of calorific value, the water-saturated gas is a better reference state than the dry gas. (In any custody transfer it is necessary to identify which reference state is used. This document provides factors for converting between dry and water-saturated gas.)

Metric and U.S. Customary reference conditions

Both the temperature and pressure are different in the ANSI/ASTM/API reference conditions (60 °F, 14.73 Psi; 288.71 K, 101.560 kPa) and in the ISO/ANSI/ASTM metric reference conditions (288.15 K, 101.325 kPa). Conversion of a molar thermodynamic property of an ideal gas from one reference condition to the other requires correction only for temperature. For volumetric properties there are both temperature and pressure corrections. For properties of real gases there always are both temperature and pressure corrections.

Appendix 7. Thermodynamic data: their sources and uncertainties

7a. Sources of thermodynamic data

Heat capacity and enthalpy increment

Standard heat capacities at constant pressure and at 298.15 K for the substances in Tables 3 and 4 are taken from Table A7a which summarizes an evaluation by Wilhoit [1][*]. These are selected instead of those of Rossini et al. [2] because they are based on more recent and more detailed calculations. Wilhoit has presented his results in the form of polynomials of degree two that are valid in the temperature range from 268 to 308 K. The constants of the polynomials, a reference to the method of calculation of C_p and the value of C_p^o (298.15 K) calculated from the polynomial are presented in Table A7a.[**]

The polynomials have the dimensionless form:

$$C_p^o/R = a + b\ (T\text{-}273.15\ \text{K}) + c(T\text{-}273.15\ \text{K})^2$$

in which the values of a, b, c are determined by the method of least squares to fit the data given in the references.

The enthalpy difference is calculated from C_p^o as

$$H(T_2) - H(T_1) = \int_{T_1}^{T_2} C_p^o\ dT$$

$$= R \int_{T_1}^{T_2} [a + b(T\text{-}273.15\ \text{K}) + c(T\text{-}273.15\ \text{K})^2\ dT$$

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[*] References are listed at the end of the appendix.

[**] Tables A7a through A7f are at the end of Appendix 7a.

$$H°(T_2) - H°(T_1) = R[a(t_2 - t_1) + (b/2)(t_2^2 - t_1^2) + (c/3)(t_2^3 - t_1^3)]$$

where $t = T - 273.15$ K, i.e. the Celsius temperature.

The values of C_p (298.15 K) in Tables 3, 4 and A7a differ by less than 1 J mol^{-1} K^{-1} from those given by Rossini et al. [2] and by Stull, Westrum and Sinke [3], except for 2-methylpentane, 1.84; 3-methylpentane, 2.89; cyclobutane, 1.36; cyclohexane, 1.02; and benzene, -3.91 J $mol^{-1}K^{-1}$. In the last case, the maximum difference the use of the polynomial would cause in the tabulated enthalpy of combustion is 0.04 kJ mol^{-1} (in approximately 3303 kJ mol^{-1}); or 1.2×10^{-5} relative error in the enthalpy of combustion. This is considered to be well within the uncertainty of the measured enthalpy of combustion.

Enthalpies of formation

The values of $\Delta_f H°$(298.15 K) for the auxiliary substances in Table 3 were taken from the recent recommendations of the CODATA Task Group on Key Values for Thermodynamics [15]. These do not differ significantly from those given by Wagman et al., [16], and (except possibly for H_2S) may be expected to be used in the next generation of chemical thermodynamic tables and to be used internationally.

Enthalpy of combustion

The selected values of the standard molar enthalpy of combustion at 298.15 K of each gaseous substance are listed in Table A7b (and are repeated in Table 4). These are taken from an evaluation by Domalski [17,18b] and have been previously published by Armstrong, Domalski and Minor [18a]. If the enthalpy of combustion of the gas depends upon measurements made on the liquid, $\Delta_c H°$ for the liquid is also given. For each value, references are given to the source of the data used in making the selection as well as others examined but not used. The agreement of this selected value with those in several compilations of critically evaluated data is also shown. In most cases, the values presented here are consistent with those in the API tables [2] and their successors [76,77].

Methane is considered here in slightly more detail than the other hydrocarbons, both because of its importance in natural gas and also as an illustration of the problems that must be faced when selecting a "best value."

The sources of original measurements of enthalpy of combustion for methane are given in Table A7c in chronological order. These eight studies provide the entire measurement set. (There are fewer for some of the other hydrocarbons.) Because of the great increase in experimental accuracy and precision in the early 20th century, only the three measurements reported after 1930 are of any importance. Of these, only the studies of Rossini [55] and of Pittam and Pilcher [48] are considered today, because of the method used and the higher precision of measurement.

Those two sets total to 12 experiments, the values for which, corrected to 298.15 K and ideal conditions, are listed in Table A7d. The results of the two studies overlap, their precisions (separately) are similar, and it is not clear that any of the points can be discarded. If there were no other considerations, it would be appropriate to pool the data and take an average: 890.65 kJ mol^{-1}. There are, however, several additional points to be considered.

1. The impurity level of the synthetic methane used by Pittam and Pilcher was less than 5 ppm*. Rossini also used a sample of synthetic methane with a measured 1219 ppm impurity of CO, for which a correction was made. The NBS reference sample of methane (83), from a natural gas source and with a 400 ppm

*We are indebted to Prof. H. A. Skinner for information about this sample.

ethane impurity, has about the same enthalpy of combustion as that reported by Pittam and Pilcher (using Rossini's value for methane).

2. Pittam and Pilcher measured CO_2 production to determine the extent of reaction, a preferred method, while Rossini measured water production. Both used flow calorimetry, with about the same precision. Pittam and Pilcher's value depends, via their calibration, on Rossini's measurement of the enthalpy of formation of water (adding to the uncertainty) while Rossini's value for methane does not.

3. Both Rossini and coworkers (39,50,51,52,55,56) and Pilcher and coworkers (47,48) have measured the enthalpies of the C_1 to C_6 hydrocarbons. There is overlap with studies by Good (31,32). There does not seem to be any systematic difference separating the work in Rossini's laboratory and that in Pilcher's, but there may be more scatter in the earlier work.

4. Correlations of enthalpies of formation for the alkanes favor the more uniform values (with respect to the increment for CH_2) of Pittam and Pilcher and may favor a value for methane that is between those of the two studies. The latter may be more of an evaluator's decision than a property of the correlations: methane occupies a unique position.

A preliminary analysis of these four factors indicates that both studies should be considered in a reassessment. Neither outranks the other. An average value of 890.6 ± 0.7 kJ mol^{-1} (2σ uncertainty) is an appropriate choice, considering methane alone.

In our opinion, however, there should be a thorough-going reassessment of the thermodynamic properties of the lower alkanes as a group before any, probably small, readjustments are made. Somayajulu et al. [98] have suggested a possible revision. It is probable, however, that an improvement can come only from new, highly accurate measurements. There also are additional considerations that are related more to gas technology than to the combustion experiments.

5. Recording flow calorimeters that are commonly used in determining heating values are calibrated against samples of methane for which the heating values are certified. In the U.S.A., and possibly elsewhere, these certifications are now based on analysis of the gas and calculation of the heating value, using procedures outlined in this document. If the enthalpy of combustion of methane is revised, a plan must be developed to (a) recertify the standard samples and (b) recalibrate the calorimeters (or revise the calibration factors now in use). It would be advisable to develop this plan now and have it agreed upon by the various standards-setting and user groups.

6. Based on existing measurements a revision of the enthalpy of combustion of methane would be to a value that lies within the uncertainty (2σ) of the present recommendation and the new value would have an equally large uncertainty. It may then be questioned whether a new value, strongly overlapping with the old one, should be introduced in technical practice.

Because of these last two factors and the desirability of a reassessment of the lower alkanes as a group, we have retained the older value which is the basis for many existing tables of calorific values. When a revision is made of $\Delta_c H(298.15\ \mathrm{K})$ for any of the gases of interest here, the procedures given in this document and data in the tables will permit straightforward calculation of new heating values at the various reference conditions.

Compiled data on methane

Several compilers, have reevaluated the original data and have reported values (primary compilations). Others have adopted and applied these results (secondary compilations). The more significant compilations of both types are listed in Table A7e, together with the reported value for methane (converted to SI units if originally given in other units).

Except for the selection by Pedley and Rylance [45] all of these values can be traced to Rossini's measurements [55] usually via the API tables [2,76,77]. Slight differences reflect different reanalyses, weighting, rounding procedures or variant auxiliary data. In the light of the spread of the data they are immaterial.

In this same table is listed the atomic mass scale used by each compilation, if it could be identified. If not, the most recent scale with which molecular masses are consistent is indicated. The atomic mass scale designations are keyed to Table A5a.

Vapor pressure of water

The values used here are given in Table A7f for each of the reference temperatures. The correlation equation given in the table may be used for other temperatures in the same range.

Table A7a. Heat capacity equations for auxiliary substances and hydrocarbons for the range 268 to 308 K for the equation $C_p^o/R = a + b(T - 273.15\ \mathrm{K}) + c(T - 273.15\ \mathrm{K})^2$ [1]*

Compound	Formula	a	$100b$/K	$10^5c/\mathrm{K}^2$	$C_p(298.15\ \mathrm{K})$ / $\mathrm{J\ mol^{-1}\ K^{-1}}$	Reference
methane	$CH_4(g)$	4.1947	0.3639	1.49	35.71	[4]
ethane	$C_2H_6(g)$	5.9569	1.377	1.69	52.48	[5][a]
propane	$C_3H_8(g)$	8.2671	2.286	1.90	73.59	[5][a]
n-butane	$C_4H_{10}(g)$	11.109	2.875	1.82	98.44	[6]
2-methylpropane	$C_4H_{10}(g)$	10.824	3.153	0.82	96.59	[6]
n-pentane	$C_5H_{12}(g)$	13.587	3.288	2.98	119.96	[7][b]
2-methylbutane	$C_5H_{12}(g)$	13.412	3.540	1.40	118.94	[7][b]
2,2-dimethyl-propane	$C_5H_{12}(g)$	13.584	3.846	0.45	120.96	[7][b]
n-hexane	$C_6H_{14}(g)$	16.134	3.986	3.60	142.62	[7][b]
2-methylpentane	$C_6H_{14}(g)$	16.064	4.172	2.21	142.35	[7][b]
3-methylpentane	$C_6H_{14}(g)$	15.768	4.351	1.11	140.20	[7][b]
2-2-dimethyl-butane	$C_6H_{14}(g)$	15.877	4.579	0.52	141.55	[7][b]
2,3-dimethyl-butane	$C_6H_{14}(g)$	15.739	4.139	1.77	139.56	[7][b]
cyclopropane	$C_3H_6(g)$	6.100	2.285	2.33	55.59	[1][c]
cyclobutane	$C_4H_8(g)$	7.769	2.942	2.92	70.86	[1][c]
cyclopentane	$C_5H_{10}(g)$	8.966	4.101	0.82	83.11	[8]
cyclohexane	$C_6H_{12}(g)$	11.490	4.600	3.00	105.25	[1][c]
ethyne	$C_2H_2(g)$	5.063	0.985	-1.59	44.06	[1][c]
ethene	$C_2H_4(g)$	4.880	1.024	1.50	42.78	[9]
propene	$C_3H_6(g)$	7.277	1.858	0.80	64.41	[10]
benzene	$C_6H_6(g)$	9.435	3.371	2.46	85.58	[11]
helium	He(g)	2.500	0.000	0.00	20.78	[1][d]
argon	Ar(g)	2.500	0.000	0.00	20.78	[1][d]
oxygen	$O_2(g)$	3.520	0.044	0.28	29.37	[12][e]
hydrogen	$H_2(g)$	3.433	0.155	-0.74	28.83	[12][e]
nitrogen	$N_2(g)$	3.502	0.006	0.00	29.13	[13]
hydrogen sulfide	$H_2S(g)$	4.070	0.118	0.28	34.10	[12]
sulfur dioxide	$SO_2(g)$	4.707	0.439	0.13	40.06	[12]
carbon monoxide	CO(g)	3.503	0.009	0.09	29.15	[12]
carbon dioxide	$CO_2(g)$	4.324	0.580	-0.65	37.12	[14]

[a] Recalculated from the partition coefficient of the molecule, using procedures and molecular parameters in the reference.

[b] Calculated using the procedure in the reference.

[c] Unpublished calculations from the molecular partition function.

[d] $C_p^o = 2.5\ R$ for the monatomic gas at temperatures such that kT is well below the first excited electronic state.

[e] Either taken directly from the table in the reference or recalculated from the partition function using the same parameters as used for the tables.

*References for this table are given at the end of the appendix.

Table A7b. Enthalpies of combustion of selected hydrocarbons and sources of the data

Substance	$-\Delta_c H(298.15\ \mathrm{K})^a$ kJ mol^{-1}	Data Sources[b,c,d,e]
methane	890.31 ± 0.31	from 17, $\underline{\underline{55}}$, 61, (19,30,41,69,70), $\underline{48}$, C: =2, =3, =28, ≠45, =77
ethane	1559.84 ± 0.46	from 17, $\underline{\underline{56}}$, (23,70), $\underline{48}$, C: =2, =3, =28, ≠45, =77
propane	2219.90 ± 0.54	from 17, $\underline{\underline{56}}$, (23,70), $\underline{48}$, C: =2, =3, =28, ≠45, =77
n-butane	2877.25 ± 1.2	from 17, $\underline{\underline{56}}$, $\underline{\underline{50}}$, $\underline{48}$, C: =2, =3, ≠28, ≠45, =77
2-methylpropane	2868.72 ± 2.0	from 18b, $\underline{\underline{57}}$, $\underline{\underline{50}}$, $\underline{\underline{46}}$, (70), $\underline{48}$, C: =2, =3, ≠28, ≠45, =77
n-pentane	3535.77 ± 0.5 (g) 3509.04 ± 0.5 (ℓ)	from $\underline{\underline{32}}$, $\underline{\underline{47}}$, $\underline{\underline{52}}$, $\underline{\underline{44}}$ (vap), 56, 60, C: ≠2, ≠3, =18a, =28, =45, ≠77
2-methylbutane	3528.87 ± 0.4 (g) 3503.64 ± 0.4 (ℓ)	from $\underline{\underline{32}}$, $\underline{\underline{47}}$, $\underline{\underline{39}}$, $\underline{\underline{63}}$(vap), 60, 62, C: ≠2, ≠3, ∿28, =45, ≠77
2,2-dimethylpropane	3514.60 ± 0.6 (g) 3492.22 ± 0.6 (ℓ)	from $\underline{\underline{32}}$, $\underline{\underline{47}}$, $\underline{\underline{39}}$, C: ≠2, ≠3, ≠28, ∿45, ≠77
n-hexane	4194.75 ± 0.6 (g) 4163.12 ± 0.6 (ℓ)	from 18b, $\underline{\underline{31}}$, $\underline{\underline{52}}$, $\underline{\underline{34}}$, $\underline{\underline{44}}$(vap), 71(vap), (68,=74, 65) C: =2, =3, =28, =45, =76, ∿77
2-methylpentane	4187.64 ± 1.0 (g) 4157.68 ± 1.0 (ℓ)	from 18b, $\underline{\underline{51}}$, $\underline{\underline{44}}$(vap), 71(vap), C: =2, =3, =28, =45, =76, ∿77

Table A7b (cont'd)

Substance	$-\Delta_c H(298.15\ K)$[a] kJ mol^{-1}	Data Sources[b,c,d,e]
3-methylpentane	4190.32 ± 0.9 (g) 4159.94 ± 0.9 (ℓ)	from 18b, 51, 44(vap), 71(vap), C: =2, =3, =28, =45, =76, ∿77
2,2-dimethylbutane	4176.34 ± 1.0 (g) 4148.52 ± 1.0 (ℓ)	from 18b, 51, 44(vap), 38(vap), C: =2, =3, =28, =45, =76, ≠77
2,3-dimethylbutane	4184.17 ± 0.9 (g) 4154.92 ± 0.9 (ℓ)	from 18b, 51, 44(vap), 71(vap), (69, 70), C: =2, =3, =28, ≠45, =76, ≠77
cyclopropane	2091.37 ± 0.5	from 17, 40, (21, 23, 29) C: =3 =28, =45
cyclobutane	2745.16 ± 0.5 (g) 2720.52 ± 0.5 (ℓ)	from 18b, 35 = 26, 54(vap), C: ≠3, ≠28, ≠45, ≠77
cyclopentane	3319.59 ± 0.8 (g) 3290.93 ± 0.8 (ℓ)	from 17 & 18b, 33, 8(vap), 35, 64, (68 = 74), C: =2, =3, =28, ≠45, =77
cyclohexane	3952.96 ± 0.7 (g) 3919.86 ± 0.7 (ℓ)	from 17 & 18b, 31, 33, 44(vap), ∿35, ∿64, ∿43, (68 = 75, 59, 66, 67), C: =2, ∿3, =28, =45, =77
ethyne	1299.59 ± 0.8	from 17, 72 = 25, (21, 23, 41, 42), C: =2, =3, ≠28, ≠45, =77
ethene	1410.97 ± 0.4	from 17, 58, 53 = 36, ∿78, 79 (19, 21, 23, 29, 30, 41, 42) C: =2, =3, ≠28, ≠45, =76, ≠77

Table A7b (cont'd)

Substance	$-\Delta_c H(298.15\ K)$[a] kJ mol^{-1}	Data Sources[b,c,d,e]
propene	2058.44 ± 0.6	from 18b, $\underline{\underline{58}}$, $\underline{\underline{37}}$, $\underline{\underline{73}}$, ∿51, (21, 23, 69, 70), C: =2, =3, ≠28, ≠45, =77
benzene	3301.51 ± 0.5 (g) 3267.71 ± 0.5 (ℓ)	from 2 & 17, $\underline{\underline{31}}$, $\underline{\underline{49}}$, 44(vap), 27, C: =2, =3, =28, =45, =77

[a]The uncertainty is that given in the source from which the value has been taken. See Appendix 7b for those assigned here.

[b]References are given in the list at the end of this appendix.

[c]References are marked to show how data in them were used or correspond to the selected values "from 10" - the value was taken from reference 10. 17 (double underline): used in making the selection (in the source cited); $\underline{20}$: recent value, not used but to be considered in new evaluations; 31 (unmarked): examined but not used: =2; same value; ∿7: approximately the same; ≠3; not the same value; (17): not used, of historical interest only; C: compilations of data follow this sign.

The entry for n-pentane should be read as follows. The selected value was taken from [32]. It was based on data in [32, 47, 52 and 44], the last being for the vaporization enthalpy. References [56] and [60] were not used. The present value agrees with the compilations [18a], [28] and [45], while it differs from [2], [3] and [77].

[d]Some references not cited in the sources quoted have been added during the preparation of this table. They are mainly for enthalpy of vaporization and for compilations of data.

Table A7b (cont'd)

[e]Three references are to the API project 44 tables and successors: [2], (1953) [76], (1967); [77], (1981). The 1967 version is cited only of the other two are significantly different.

Table A7c. Heating value of methane - sources of data

Experimental Measurements		$-\Delta_c H°(298.15\ K)/kJ\ mol^{-1}$	
A.	Andrews, 1848 [19]	[883.6]	a
B.	Favre and Silberman 1852 [30]	[864.1]	a
C.	Thomsen, 1880, 1886, [69,70]	887.0 ± 3	b
D.	Berthelot, 1881, [21]	892.3 ± 9	b
E.	Mixter, 1901, [41]	[888.6]	c
F.	Rossini, 1931, [55]	890.31 ± 0.6	d
G.	Roth and Banse, 1932, [61]	891.8 ± 2.	e
H.	Pittam and Pilcher, 1972, [48]	890.71 ± 0.8	f

Notes for Table A7c

[a]Not comparable to the later measurements. Corrected from ~15 °C by comparison to authors' measurements of $\Delta_f H(H_2O,\ell)$.

[b]As recalculated by Rossini [55] to 30 °C and corrected by us to 25 °C.

[c]From heat of decomposition, in the presence of acetylene. Corrections are approximate.

[d]Uncertainty is precision only, 2σ. Corrected from 30 °C to 25 °C.

[e]As recalculated by Cox and Pilcher [28].

[f]Uncertainty is precision only, 2σ.

Table A7d. Data points and statistics for studies of methane by Rossini and by Pittam and Pilcher

Author	$-\Delta_c H°(298.15\ K)/kJ\ mol^{-1}$ Individual Points	Averages
Rossini [55][a]	891.823[b]	
Pittam and Pilcher [48][c]	891.23	
Pittam and Pilcher	891.17	Ave (P&P): 890.71 ± 0.43[d]
Rossini	890.633	Ave (12 pts): 890.65 ± 0.37
Pittam and Pilcher	890.62	
Pittam and Pilcher	890.61	Ave (R-6 pts): 890.56 ± 0.66
Rossini	890.503	Ave (11 pts): 890.52 ± 0.27
Pittam and Pilcher	890.36	
Pittam and Pilcher	890.34	
Rossini	890.340	Ave (R-5 pts): 890.31 ± 0.33
Rossini	890.061	
Rossini	890.013	

[a] $\Delta_c H(298.15\ K)$ = tabulated points in [55] $-0.613\ kJ\ mol^{-1}$.

[b] Rejected by Rossini, a reasonable decision with only his set to consider, but borderline for the combined set.

[c] $\Delta_c H°(298.15\ K)$ = tabulated points in [48] $-0.02\ kJ\ mol^{-1}$.

[d] Uncertainties are 95% confidence level for the mean but for precision only.

Table A7e. Enthalpy of combustion of methane as an ideal gas and relative atomic mass scales given in compilations of thermochemical data

Compilation	Atomic Mass Scale[a]	$-\Delta_c H°(298.15\ K)$[b] / $kJ\ mol^{-1}$
International Critical Tables (1929) [87]	1923 (G)	882.37
NBS Circular C461 (1947) [88]	1941 (F)	890.35
NBS Circular C500 (1952) [89]	1941 (F)	890.35
Rossini et al. (1953) [2] (API Project 44)	1941 (F)	890.35[c]
Landolt-Bornstein (1961) [90]	1953 (E)[d]	890.36[c]
NBS Tech. Note 270-3 (1968) [16]	1961 (D)	890.36
Stull, Westrum, Sinke (1969) [3]	1941 (F)	890.34[c]
Cox, Pilcher (1970) [28]	1961 (D)	890.32
JANAF Thermochemical Tables (1971) [81]	1961 (D)	890.33
ASTM DS4A (1971) [97]	1969 (C)	890.36[c]
Domalski (1972) [17]	1961 (D)	890.31
NBS Tech. Note 653 (1974) [91]	1969 (C)	---
NBS Tech. Note 684 (1976) [92]	1969 (C)	---
ASTM D-3588 (1977) [93]	1971 (B)	890.36[c]
Pedley, Rylance (1977) [45]	1971 (B)	890.7
GPA Publication 2145-77 (1977) [94a]	1961 (D)	890.40[c,e]
CODATA Key Values (1978) [95]	1969 (C)	---
Robie, Hemmingway, Fisher (1978) [95]	1971 (B)	890.36[c]
GPA Publication 2145-SI-80 (1980) [94b,c]	1969 (C)	890.33[c,e]
GPA Engineering Data Book (1980) [96]	1969 (C)	890.33[c,e]
This work	1981 (A)	890.31

[a] Year the scale was established and the code given in Table A5a.

[b] Values reported in other units or at other temperatures have been converted using factors in this document.

[c] Value for methane taken from another compilation.

[d] Physical scale $^{16}O = 16$ indicated without elaboration. Atomic mass scale may be earlier than 1953. Reported enthalpy has been multiplied by 4.184/4.1855 to convert to current absolute joules.

[e] Calculated from values at 288.15 K or 288.71 K from enthalpies of combustion in $MJ\ m^{-3}$ using thermodynamic properties developed in this work. Values in $MJ\ kg^{-1}$ in the same sources are in error.

Table A7f. Vapor pressure of water, $p(H_2O)$, used in this document

T/K	$p(H_2O)$/Pa[a]
273.15	611.213
288.15	1705.32
288.706	1767.34
298.15	3168.74

[a]Using the 1968 International Practical Temperature Scale and the Vapor Pressure Equation [84]:

$$\ln p(H_2O) = \sum_{i=o}^{6} g_i T_{68}^{i-2} + g_7 \ln T_{68}, \text{ where}$$

$g_0 = -0.29912729 \times 10^4$, $g_1 = -0.60170128 \times 10^4$,
$g_2 = 0.1887643854 \times 10^2$, $g_3 = -0.28354721 \times 10^{-1}$,
$g_4 = 0.17838301 \times 10^{-4}$, $g_5 = -0.84150417 \times 10^{-9}$,
$g_6 = 0.44412543 \times 10^{-12}$, and $g_7 = 0.2858487 \times 10^1$.

Appendix 7b. Uncertainties in thermodynamic quantities

<u>Uncertainties in the standard enthalpies of combustion at T = 298.15 K</u>

Cox and Pilcher [28], Good [32], Domalski [18a], Pedley and Rylance [45] and Chao [80] have estimated uncertainties in some or all of the standard enthalpies of combustion or the enthalpies of formation at T = 298.15 K of the hydrocarbons listed in Table 4. Their estimates are given in Table A7g. Where necessary these have been converted to kilojoules per mole.

The selected uncertainties s_c and relative uncertainties $s_c/\Delta_c H°$ for this work are listed in the right hand columns of Table A7g. They are considered to represent 95 percent confidence limits for the values of $\Delta_c H°$ at 298.15 K.

When the enthalpy of formation is derived from the enthalpy of combustion, the estimated uncertainty in the enthalpy of formation s_f is related to the estimated uncertainty in the enthalpy of combustion s_c by the relationship

$$s_f^2 = s_c^2 + [as_f(CO_2)]^2 + [(b/2)s_f(H_2O)]^2$$

where $s_f(CO_2)$ is 0.13 kJ mol^{-1}, $s_f(H_2O)$ = 0.042 kJ mol^{-1} and a and b give the stoichiometric coefficients in the equation of combustion.

$$C_aH_b + (b/4 + a)O_2 = aCO_2 + (b/2)H_2O$$

Because $s_f(CO_2)$ and $s_f(H_2O)$ are substantially smaller than s_f or s_c for the hydrocarbons the difference s_f - s_c is generally quite small. The sign of the difference depends on whether s_f is derived from s_c or vice versa. Typical differences may be found in the column labeled C&P in Table A7g. For the purpose of this discussion, little distinction will be made between s_f and s_c. However s_c is used preferentially if it is available.

Table A7g. Estimates of uncertainties s_c in enthalpy of combustion or s_f in enthalpy of formation by various authors

	C&P		G	D	P&R	Chao	This Work	$10^4 s_c$
	s_f	s_c	s_c	s_c	s_c	s_c	s_c	$\frac{}{\Delta_c H^o}$
				kJ mol^{-1}				
methane	0.29	0.25	-	0.29(.50)	0.4	0.50^b	0.62	7.0
ethane	0.50	0.46	-	0.46	0.2^b	0.59^b	1.01	6.5
propane	0.59	0.54	-	0.54	0.3	0.63^b	1.02	4.6
n-butane	0.67	0.63	-	1.26	0.6	0.67^b	1.44	5.0
2-methlypropane	0.54	0.46	-	2.09(1.26)	0.5	-	1.44	5.0
n-pentane	0.63	(0.63)	0.46	0.46	0.7	-	0.46	1.3
2-methlybutane	0.63	(0.63)	0.46	0.46	0.6	-	0.46	1.3
2,2-dimethylpropane	1.05	0.96	0.50	0.63	0.7^b	-	0.50	1.4
n-hexane	0.75	(0.75)	-	0.63^a	0.4	-	0.63	1.5
2-methylpentane	1.00	0.92	-	1.05^a	0.9	-	1.05	2.5
3-methlypentane	1.00	0.92	-	1.05^a	0.9	-	1.05	2.5
2,2-dimethylbutane	1.00	0.92	-	0.96^a	0.8^b	-	0.96	2.3
2,3-dimethylbutane	1.00	0.92	-	0.92	0.7^b	-	0.92	2.2
cyclopropane	0.59	0.54	-	-	0.5	-	0.54	2.8
cyclobutane	0.59	0.50	-	-	0.5^b	-	0.50	1.8
cyclopentane	0.84	0.71	-	-	0.8^b	-	0.71	2.1
cyclohexane	0.63	(0.63)	-	-	0.3^b	-	0.63	1.6
ethyne	0.79	0.63	-	-	1.0	-	0.63	4.8
ethene	0.42	(0.42)	-	-	1.2^b	-	0.42	3.0
propene	0.67	(0.67)	-	-	0.4	-	0.67	3.2
benzene	0.54	(0.54)	-	-	0.3^b	-	0.54	1.6
oxygen								
carbon dioxide							0.13	-
water (liquid)							0.042^b	-

Parentheses in the C&P column indicates that s_c was set equal to s_f (for which a value is given)

[a]Value for gas phase combustion is taken as the same as for the liquid.

[b]Indicates the value for s_f is used.

Code to heading: C&P, Cox and Pilcher [28]; G, Good [32]; D, Domalski [18b]; P&R, Pedley and Rylance [45], Chao [80].

The following procedure was used in arriving at the estimated uncertainties s_c (this work) given in Table A7g. Two tests were made for the normal hydrocarbons C_1 to C_4. Both combine estimates of accuracy made by evaluators with the spread between the means of the two sets of experiments. The uncertainties of Domalski and Chao were averaged and added quadratically to the difference between the average values of $\Delta_c H°$ presented by Domalski [18b] and by Pittam and Pilcher [48]. Domalski's estimate of s_c for methane was considered to be low as a result of the difference 0.4 kJ mol^{-1} between the work of Pittam and Pilcher and the previously accepted values for methane. Therefore, Chao's estimate alone was used in the quadratic addition.

Table A7h. Estimated total uncertainties - first test

Substance	s_c/kJ mol^{-1}			s_c/kJ mol^{-1}	$10^4 s_c/\Delta_c H°$
	Chao	D	Δ	this work	
methane	0.50	(0.29)0.50	0.40	(0.56)0.64	7.2
ethane	0.59	0.46	0.86	1.01	6.5
propane	0.63	0.54	-0.73	0.94	4.2
n-butane	0.67	1.26	0.29	1.01	3.5

The results are summarized in Table A7h above, in which s_{Chao} and s_D represent the two estimated errors, Δ represents the difference between the values selected by Domalski (these tables) and the results presented by Pittam and Pilcher. The value of s_c is calculated as

$$s_c = [\{(s_{Chao} + s_D)/2\}^2 + \Delta^2]^{\frac{1}{2}} .$$

This has been reduced to a relative uncertainty in the last column.

A second test was made, and this was applied also to 2-methylpropane. In this test, the uncertainties listed by Domalski were summed quadratically with the uncertainties listed by Pittam and Pilcher for their combustion experiments and the values of Δ. This value is

$$s_c = (s_D^2 + s_{PP}^2 + \Delta^2)^{\frac{1}{2}}$$

The data, the values of the square root of the sum of squares and the relative uncertainties are given in Table A7i.

Table A7i. Estimated total uncertainties - second test

substance	$-\Delta_c H°$	s_c	$-\Delta_c H°$	s_c	Δ	$(\Sigma^2)^{\frac{1}{2}}$	$\frac{10^4(\Sigma^2)^{\frac{1}{2}}}{\Delta_c H°}$
			kJ mol^{-1}				relative
	Domalski		Pittam and Pilcher				
CH_4	890.31	0.29	890.71	0.38	0.4	0.62	7.0
C_2H_6	1559.84	0.46	1560.69	0.25	0.86	1.01	6.5
C_3H_8	2219.90	0.54	2219.17	0.46	-0.73	1.02	4.6
n-C_4H_{10}	2877.25	1.26	2877.54	0.63	0.29	1.44	5.0
i-C_4H_{10}	2868.72	1.26 (2.09)	2869.00	0.59	0.28	1.42	5.0

This calculation gives a reasonably uniform set of absolute and relative uncertainties and is adopted for the data presented for these compounds in this document as shown in the right hand columns of Table A7g. Here again an adjustment was made to Domalski's estimate of s_c for 2-methlypropane. He had given a large estimate based on disagreement between two sets of combustion measurements made by Rossini [57] and Prosen, Maron and Rossini [50]. The later results of Pittam and Pilcher eliminate the earlier measurements by Rossini from further consideration. On this basis the uncertainty for Domalski's average value for 2-methlypropane was reduced to the same uncertainty for n-butane for this calculation.

For the pentanes, the uncertainties estimated by Good [32] were considered to be appropriate and were adopted without change.

For the hexanes, the estimates of uncertainty made by Domalski [18b] are used. For the cyclic and unsaturated hydrocarbons the uncertainties given by Cox and Pilcher [28] are used.

Uncertainties in heat capacities and enthalpies

For all of the alkane hydrocarbons, Scott, [7], presents values of C_p for which he gives the first uncertain figure to be at the hundredths cal mol^{-1}K^{-1}. On this basis, we infer $s(C_p) < 0.05$ cal mol^{-1}K^{-1} which would be $s(C_p) < 0.21$ J mol^{1}K^{-1}. Over the range 273.15 K to 298.15 K this amounts to an error of $H(T) - H(298.15\ \mathrm{K}) < 25 \times 0.21$ J mol^{-1}K^{-1} (5.2 J mol^{-1}K^{-1}). We adopt the conservative position that $s\{H(T) - H(298.15)\} = 5.2$ J mol^{-1}K^{-1} for all the hydrocarbons.

In Scott [7] individual uncertainties in the heat capacities of the hydrocarbons are given four ways: as $s(C_p$, observed), $s(C_p$, calculated), $\Delta(C_p$ obs - C_p calc), and statistical uncertainty at 298.15 K calculated from the appropriate variance-covariance matrix.

Table A7j. Estimated uncertainties in C_p^o of hydrocarbons from Scott's [7] correlation of thermodynamic functions

Substance	T/K	Uncertainties at T/K $s(C_p$,obs)	$s(C_p$,calc)	$\Delta(C_p$,obs-calc)	at 298.15 K $s(C_p$,matrix)
		10^2 J mol^{-1}K^{-1}			
propane	293.15	17	8	71	8
n-butane					4
2-methylpropane	273.15	17	8	21	13
n-pentane	298.15	25	8	4	8
2-methylbutane	317.2	25	21	4	37
2,2-dimethylpropane	298.15	25	25	8	25
n-hexane	333.85	29	13	13	17
2-methylpentane	325.10	29	17	46	17
3-methylpentane	332.10	29	25	21	42
2,2-dimethylbutane	341.55	33	17	8	29
2,3-dimethylbutane	341.60	33	21	4	71

Scott recommends that the uncertainties in the heat capacities be taken as twice the values listed. We have taken twice the values listed as the entries in the column headed $s(C_p^o$,obs), and these are listed in Table 15.

Table A7k. Comparative calculations of C_p^o

		Wilhoit [1]	Scott[7]	Gurvich[82]	JANAF[81]	Wagman[16]	Angus[9,10]
		C_p^o/J mol^{-1}K^{-1}					
	CH_4	35.71	(35.68)*	35.695	(35.64)	(35.31)	35.71
	C_2H_2	44.06		44.036	(44.095)	(43.93)	
	C_2H_4	42.88		42.882	(42.89)	(43.56)	42.88
	C_2H_6	52.47	(52.59)	52.486	(52.63)		
	C_3H_8	73.59	(72.96)				
cyclo	C_4H_8	70.86					
n	C_4H_{10}	98.44	(97.49)				
i	C_4H_{10}	96.59	(96.77)				
cyclo	C_5H_{10}	83.11					
n	C_5H_{12}	119.96	(120.04)				
1-me	C_5H_{12}	118.95	(118.86)				
2,2	C_5H_{12}	120.96	(120.83)				
cyclo	C_6H_{12}	105.25					
n	C_6H_{14}	142.62	(142.59)				
2-me	C_6H_{14}	142.25	(142.21)				
3-me	C_6H_{14}	140.20	(140.12)				
2,2	C_6H_{14}	141.55	(141.46)				
2,3	C_6H_{14}	139.56	(139.41)				
	C_6H_6	85.58					
	O_2	29.37		29.378	(29.37)	(29.35)	
	CO_2	37.12		37.135	(37.13)	(37.11)	37.13
	H_2	28.83		28.836	(28.836)	(28.824)	
	C			8.536	(8.527)	(8.527)	

*Values in parentheses have been converted from other units.

There are slightly different calculated values of C_p in various compendia. They are compared in Table A7k. The differences are due largely to choices of molecular parameters, choices of energy differences between conformers and the calculational models. The differences are small and ignored here.

Uncertainty in the vapor pressure of water

The uncertainty of the vapor pressure of water has several aspects: (1) the uncertainty with which the vapor pressure has been experimentally determined, which is taken by us as the uncertainty in the partial pressure of water vapor in the water saturated ideal-gas fuels; (2) the deviation of the vapor pressure of water from its standard value when in the presence of hydrocarbons; (3) the degree to which true saturation is achieved in real-gas mixtures measured under "saturated" conditions. The third aspect above is a measurement problem encountered in the field that must be treated as a separate issue. For the purposes of this document we assume uncertainty (1) to be $s(p,H_2O) = 1$ Pa. While Wexler [84] does not specifically state estimates of uncertainty, he compares his formulation with measurements by Douslin [85] and Besley and Bottomly [86] and finds differences not exceeding 1.3 Pa in the range 273.15 to 298.15 K. At $T = 273.15$ K the triple point pressure is not uncertain by more than 0.01 Pa.

Uncertainty in the relative partial pressure of fuel

Using criterion (1) for the uncertainty in the partial pressure of water, we calculate the relative uncertainty $s(p,\text{fuel})/(p,\text{fuel})$ in the partial pressure of fuel at the reference states to be 1×10^{-5}, as follows.

Taking $s(p,H_2O) = 1$ Pa and values of $s(p,\text{fuel})$ ranging from a maximum of 101.560 kPa - 0.611 kPa = 100.95 kPa at 273.15 K to a minimum of 100 kPa - 3.168 kPa = 96.83 kPa, $s(p,\text{fuel})/(p,\text{fuel})$ ranges from 9.9×10^{-6} to 10.3

$\times 10^{-6}$. Since this range is much smaller than our knowledge of the uncertainty of $p(H_2O)$, we assign a value of 10×10^{-6} for $s(p,\mathrm{fuel})/(p,\mathrm{fuel})$ for water saturated gas at all pressures and temperatures.

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Appendix 8. Relationships between thermodynamic quantities in Tables 3 and 4.

Standard Enthalpy of formation from the elements

The enthalpy of formation of a compound in Tables 3a and 3b from its elements is the enthalpy change of a process such as is illustrated below for $H_2O(1)$ and $CO_2(g)$.

$$H_2(g) + \frac{1}{2} O_2(g) = H_2O(\ell); \tag{A8.1}$$

$$C(c,graphite) + O_2(g) = CO_2(g); \tag{A8.2}$$

Similar reactions can be written for the other substances. The enthalpy change, $\Delta_f H°$, is for the process with the substances in their standard states. For example, the first reaction at 298.15 K is represented as follows

$$\Delta_f H°(H_2O,\ \ell,\ 298.15\ K) = H°(H_2O,\ \ell,\ 298.15\ K)$$
$$-H°(H_2,\ g,\ 298.15\ K) - \frac{1}{2} H°(O_2,\ g,\ 298.15K),\ p = 101.325\ Pa \tag{A8.3}$$

Information in parentheses specifies the conditions, and if the conditions are clearly stated elsewhere some of this information may be omitted as being understood. The individual $H°$ terms are not measurable, only changes in them are, e.g. $\Delta_f H°$, $\Delta_c H°$ or $[H(T_1) - H(T_2)]$.

The enthalpy of reaction (including formation) at another temperature can be calculated from that at 298.15 K using a cycle of reactions

$$\begin{array}{llllll} A & + B & \rightarrow C & + D & & T_1\ (298.15\ K) \\ \uparrow_1 & \uparrow_2 & \downarrow_3 & \downarrow_4 & & \\ A & + B & \rightarrow C & + D & & T_2 \end{array} \tag{A8.4}$$

$$\Delta_r H(T_2) = \Delta H(1) + \Delta H(2) + \Delta_r H(298.15\ \mathrm{K}) + \Delta H(3) + \Delta H(4)\ .$$

For reaction A8.1, the formation of water in its standard state, this becomes:

$$\begin{aligned}\Delta_f H°(\mathrm{H_2O,l},T_2) &= [H°(298.15\ \mathrm{K}) - H°(T_2)](\mathrm{H_2,g}) \\ &+ 0.5[H°(298.15\ \mathrm{K}) - H°(T_2)]\ (\mathrm{O_2,g}) \\ &+ \Delta_f H°(\mathrm{H_2O,l},298.15\ \mathrm{K}) - [H(298.15\ \mathrm{K}) - H°(T_2)]\ (\mathrm{H_2O,l})\ .\end{aligned} \quad (A8.5)$$

Note that all enthalpy differences have been written with T = 298.15 K first. The degree sign indicates standard state conditions. When T = 288.15 K equation A8.5 gives one of the conversions among reference conditions needed to calculate Table 3.

Inserting values from Table 3a and 3b into equation A8.5 we find:

$$\Delta H_f^{\circ}(\mathrm{H_2O,\ 1,\ 288.15\ K}) = -285.830\ \mathrm{kJ\ mol^{-1}} -0.753\ \mathrm{kJ\ mol^{-1}} + 0.288\ \mathrm{kJ\ mol^{-1}} + \frac{1}{2} \times 0.293\ \mathrm{kJ\ mol^{-1}}. \quad (A8.6)$$

$$-\Delta_f H°(\mathrm{H_2O,\ 1,\ 288.15\ K}) = 286.1485\ \mathrm{kJ\ mol^{-1}}.$$

This reproduces the value found in Table 3.

By an analogous process the enthalpy of combustion of a hydrocarbon can be determined at a different temperature. The combustion of a gaseous hydrocarbon is represented by the following equation:

$$\mathrm{C_aH_b(g)} + (\mathrm{a} + \frac{\mathrm{b}}{4})\ \mathrm{O_2(g)} = \mathrm{a\ CO_2(g)} + \frac{\mathrm{b}}{2}\ \mathrm{H_2O}(\ell), \quad (A8.7)$$

where the stoichiometric coefficients depend upon the composition of the hydrocarbon. The standard enthalpy of combustion at temperature T = 298.15 K represents the enthalpy of combustion with each reactant and each product of combustion in its standard state at the stated temperature.

The standard enthalpy of combustion depends on the temperature. The conversion of the standard enthalpy of combustion from one temperature to another will be illustrated for the combustion of methane.

$$CH_4(g) + 2\ O_2(g) = CO_2(g) + 2\ H_2O(\ell). \qquad (A8.8)$$

In this case a = 1; b = 4; b/2 = 2; and a + b/4 = 2; giving the stoichiometric coefficients for carbon dioxide, water, and oxygen, for the combustion of one mole of methane. The standard enthalpy of combustion at T = 288.15 K can be calculated from the following relationship (which is a rearrangement of equation A8.4):

$$\begin{aligned}&\Delta_c H°(298.15\ K) - \Delta_c H°(288.15\ K) = \\ &a[H°(CO_2,\ g,\ 298.15\ K) - H°(CO_2,\ g,\ 288.15\ K)] \\ &+ b/2[H°(H_2O,\ \ell,\ 298.15\ K) - H°(H_2O,\ \ell,\ 288.15\ K)] \qquad (A8.9) \\ &- (a + b/4)[H°(O_2,\ g,\ 298.15\ K) - H°(O_2,\ g,\ 288.15\ K)] \\ &- [H°(C_aH_b,\ g,\ 298.15\ K) - H°(C_aH_b,\ g,\ 288.15\ K].\end{aligned}$$

for which the required data are found in Tables 3 and 4. Using methane to illustrate the calculation we have:

$$\begin{aligned}&[\Delta_c H°(CH_4,\ g,\ 298.15\ K) - \Delta_c H°(CH_4,\ g,\ 288.15\ K)]/kJ\ mol^{-1} \\ &\quad = 0.369 + 2 \times 0.753 - 2 \times 0.293 - 0.355 = 0.934. \qquad (A8.10)\end{aligned}$$

Taking $\Delta_c H°(CH_4,\ g,\ 298.15\ K)/kJ\ mol^{-1} = -890.31$ from Table 4 we find $\Delta_c H°(CH_4,\ g,\ 288.15\ K)/kJ\ mol^{-1} = -890.31 - 0.934 = 891.244$ which rounds to -891.24.

This process is illustrated in Figure 1.

Relationship between standard enthalpy of formation, $\Delta_f H°$ and $\Delta_c H°$ for a hydrocarbon

The general reaction A8.7 can be used as the basis for calculating the standard enthalpy of formation from the elements of a hydrocarbon compound $\Delta_f H°(C_aH_b)$, if the enthalpy of combustion of the hydrocarbon is known. The relationship is:

$$\begin{aligned}\Delta_c H°(C_aH_b) &= a\ \Delta_f H°(CO_2,\ g) + (b/2)\Delta_f H°(H_2O,\ \ell) \\ &- \Delta_f H°(C_aH_b) - (a + b/4)\ \Delta_f H°(O_2,\ g). \qquad (A8.11)\end{aligned}$$

By the use of information in Tables 3b and 4b this equation may be used to calculate the enthalpy of formation of methane as an example. The temperature to which the values taken from the tables correspond must be the same for all substances involved in the equation. We use T = 298.15 K for the example.

$$\Delta_c H°(CH_4, g) = \Delta_f H°(CO_2, g) + 2\ \Delta_f H°(H_2O, l) - \Delta_f H°(CH_4, g) - 2\ \Delta_f H°(O_2, g). \qquad (A8.12)$$

Taking values from Tables 3b and 4b at T = 298.15 K, we substitute:

$$- 890.31\ \text{kJ mol}^{-1} = -393.51\ \text{kJ mol}^{-1} + 2(-285.830)\ \text{kJ mol}^{-1} - \Delta_f H°(CH_4, g) - 2(0.0). \qquad (A8.13)$$

By rearrangement and addition

$$\Delta_f H°(CH_4, g) = (+890.31 - 393.51 - 2\cdot 285.830)\ \text{kJ mol}^{-1} = -74.86\ \text{kJ mol}. \qquad (A8.14)$$

Note that all of the enthalpies of formation in this example have negative values, meaning that heat is evolved in the reaction of formation from the elements.

The converse process, the calculation of the standard enthalpy of combustion from known values of standard enthalpy of formation, uses equation A8.11 and data from Tables 3 and 4 in the same way.

Molar volume of the ideal gas

All gases, when treated as ideal gases, have the same volume per mole at the same temperature and pressure.

$$V_m^{id}(T) = RT/p$$

where R is the gas constant, p is the pressure and T is the absolute temperature. With the temperature in kelvin, pressure in pascal and volume in cubic meters, this equation becomes

$$V_m^{id} = 8.31441\ T/p\ .$$

The value for R is taken from Table 1. Numerically it is the same for cubic meter-pascal per mole-kelvin as for joule per mole-kelvin.

The amount of substance (molar) density is the reciprocal of the molar volume.

Appendix 9. Non-ideality effects and the virial equation of state

Two topics are discussed in this appendix: the procedures used to correct ideal-gas properties to those of the real gas and the selection of the virial coefficients in Table 8 (footnotes and references). Propagation of errors is discussed in Appendix 10.

<u>The virial equation of state</u>

The equation of state of a real gas is well represented by the so called virial equation of state:

$$pV_m/RT = 1 + B(T)/V_m + C(T)/V_m^2 + \dots \quad , \tag{A9.1}$$

in which the second virial coefficient is $B(T)$; the third virial coefficient is $C(T)$; V_m is the real-gas molar volume. The second virial coefficient is generally considered to represent the effects of interactions involving two molecules; the third virial coefficient, interactions involving three molecules, and so on. At the low pressures represented by the reference conditions, the second virial coefficient is adequate to represent the interactions that occur and so for this document the virial equation is truncated at the $B(T)$ term:

$$pV_m/RT = 1 + B(T)/V_m \tag{A9.2}$$

B, as well as the other virial coefficients, is a function of temperature. The errors introduced by this procedure are considered to be less than those due to the uncertainties in the values of $B(T)$ for the various substances.

The virial coefficient is used for two purposes in this document: (a) to calculate the effect of non-ideality on enthalpy of the real gas as compared to the ideal gas; and (b) to calculate the molar volume of the real gas as opposed to the molar volume of the ideal gas. This is used both in the calculation of volumetric enthalpies of combustion and in correcting enthalpies.

(a) Enthalpic effect.

The difference H-H° in the enthalpy of the real gas and the ideal gas is given by:

$$(H_m - H^\circ_m)/RT = \{B - T(\mathrm{d}B/\mathrm{d}T)\}/V_m \qquad (A9.3)$$

For the purpose of determining $T(\mathrm{d}B/\mathrm{d}T)$ it is convenient to have equations representing $B(T)$ as a polynomial in T. Equations of the form

$$B(T) = c + dT + eT^2 \qquad (A9.4)$$

have been derived and the constants c, d, and e, are given in Table A9a.

(b) Volumetric effect.

Rearrangement of equation (A9.2) gives:

$$V_m = (RT/p)\ \{1 + B(T)/V_m\}\quad , \qquad (A9.5)$$

a quadratic equation which has the solution:

$$V_m = V^\circ_m[\tfrac{1}{2} + \tfrac{1}{2}\ \{1 - 4B(T)/V_m^{id}\}^{\frac{1}{2}}] \qquad (A9.6)$$

The negative solution is ignored as being physically meaningless. V_m^{id} is a constant for a given value of p and T, and so the equation can be solved exactly if $B(T)$ is also known.

<u>Virial coefficients of mixtures</u>

Any gas has a second virial coefficient. For pure substances $B(T)$ is a characteristic physical property of the substance. For a mixture, $B(T)$ is a function of the composition as well as the pressure and temperature. Reflecting the probabilities of binary interactions between molecules, the virial coefficient of a binary mixture is given as a linear combination of terms:

$$B(\text{mixture}) = x_1^2 B_{11} + 2x_1x_2B_{12} + x_2{}^2B_{22} \qquad (A9.7)$$

in which x_1 and x_2 are the mole fractions, respectively, of components 1 and 2, for which the virial coefficients of the pure substance are B_{11} and B_{22} respectively. B_{12} represents the effect of interaction between unlike molecules.

For more complex mixtures equation (A9.7) can be generalized by taking pairwise interactions of all combinations of molecules.

$$\begin{aligned} B(\text{mixture}) = {} & x_1^2B_{11} + x_2^2B_{22} + x_3^2B_{33} + \\ & + 2x_1x_2B_{12} + 2x_1x_3B_{13} + \\ & + 2x_2x_3B_{23} + \dots \end{aligned} \qquad \text{(A9.8)}$$

For calculation of enthalpic effects and volumetric effects B(mixture) obtained in this way is used to calculate the properties of any particular mixture for which the composition $(x_1, x_2 \dots x_n)$ is known.

Most of the virial coefficients for individual substances and for binary interactions for substances and mixtures with which this document is concerned have been measured and have been compiled by Dymond and Smith [2]*.

The virial coefficients $B(T)$ for the substances in this document are listed in Table 8a. For binary mixtures involving methane as one gas, the interaction coefficients B_{12} are given in Table 8b. Because the importance of terms involving minor constituents is proportional to the products of their mole fractions, the interaction terms not involving methane have been omitted from the tables. Many of them can be found in Dymond and Smith, if necessary.

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*References are given at the end of this appendix.

Selection of virial coefficients: footnotes to Table 8.

a The uncertainties assigned to the virial coefficients from references [1] and [2] in Table 8 are those suggested by the respective authors unless otherwise stated.

b Methane virial coefficients at the required temperatures were obtained from a smooth curve through the values tabulated in reference [1].

c The values given by Dymond and Smith [2] bracket those given by Levelt Sengers et al. [1].

d Ethene values given by Dymond and Smith [2] bracket those given by Douslin and Harrison [5] which were plotted. The values of Douslin and Harrison were used at 273.15 K, 288.15 K and 298.15 K. The value at 288.71 K was interpolated from the graph.

e Ethane values given by Dymond and Smith [2] bracket those given by Douslin and Harrison [6]. The values given by Douslin and Harrison were plotted as well as those by Dymond and Smith. The values of Douslin and Harrison were used at 273.15 K and 298.15 K and values interpolated from the curve were used for other values.

f Propane values given by Dymond and Smith [2] were plotted and interpolated to give all values.

g n-Butane has been studied frequently. The selected values are interpolated on a curve drawn by eye through the points given by Dymond and Smith [2].

h The data for isobutane are scattered. Two points at 273.15 K by Jessen and Lightfoot [10] and by Das, Reed, and Eubank [11] were averaged; although they do not convert well to higher temperature data. A rough curve was drawn by eye through points from 288 K to 333 K by Kretschmer and Wiebe [12], Mason and Eakin [9]; Strein, Lichtenthaler, Schramm, and Schäfer [13], and Das, et al. [11]. This curve was used for interpolation at the other temperatures.

i The data for n-pentane are not plentiful in the temperature region below 300 K. Dymond and Smith [2] recommend values down to 300 K, and a smooth curve was drawn through them and extended to 273.4 K where a point is given by Kapello, et al. [14] whose data unfortunately drops ~ 100 $cm^3 mol^{-1}$ below the line at higher temperatures. The line passes near a point presented by Mason and Eakin [9], and somewhat above two points given by Rätzsch and Bittrich [15] and the lower limit of the smoothed data evaluated by Das, et al. [11] and below data given by McGlashan and Potter [16] and by Hajjar, et al. [17].

j For 2-methylbutane, Dymond and Smith [2] recommended values from Das et al. [8] and a curve was drawn and values interpolated.

k For 2,2-dimethylpropane a smooth curve was drawn through the data recommended by Dymond and Smith [2] and the values were interpolated.

l Benzene values were interpolated from a curve drawn from data recommended by Dymond and Smith [2].

m For 2-methylpentane the data of Waddington, et al. [7] were plotted and the curve was extrapolated below 298.15 K. One other point was given by Osborne and Ginnings [19] at 298.15 K but it was more negative by 40 cm^3 mol^{-1}.

n For 3-methylpentane the data of Waddington et al. [7] were plotted from 303 to 336 K and a curve below 300 K was extrapolated. One point at 298.15 K was given by Osborne and Ginnings [19] but it appeared to be negative by about 40 $cm^3\ mol^{-1}$.

o For 2,3-dimethylbutane the data of Waddington et al. [7] were plotted from 295 to 331 K and a curve was drawn and extrapolated. One point was determined from Osborne and Ginnings [19] but it appeared to be negative by about 40 $cm^3\ mol^{-1}$.

p For argon the uncertainties and values were recommended by Levelt Sengers, et al. [1]. A smooth curve was drawn through their recommended values and the points at temperatures other than 273.15 K were taken from the curve. The value at 273.15 K also is from [1].

q Argon plus methane, B_{12} was fitted from data listed in [2] over the range 250 to 323 K. The data of Thomas, et al. [23] and of Byrne, et al. [22] and of Belim et al. [20] fall about 6 to 8 $cm^3\ mol^{-1}$ below the rest of the data. A smooth curve was drawn through the upper data and the tabulated values were found by interpolation on the smooth curve. The value of B_{12} may be as much as 8 $cm^3\ mol^{-1}$ more negative than the tabulated values that are based on the work by Schäfer and colleagues [13, 18, 21].

r The only data given in [2] are by Mason and Eakin [9].

s Hydrogen data are smooth. A line was drawn through the data of [9] and [36] and the values used were obtained by interpolation.

t A line was drawn through the point from [38,39] listed in [2] at 248.53 K and midway between points of [38,39] at 291.4 K and [9] at 288.7 K. The values listed were obtained from the curve by interpolation.

u Ref. [2] lists only ref. [37] as a source. A slightly curved line was drawn through the two points in the range 250 to 325 K and was extrapolated to obtain the values listed.

v For ethene plus methane, B_{12} is given in [2] by Mason [9], McMath and Edmister [24], Lee and Edmister [25] which form a fairly consistent set, plus unpublished work by Lee (with Saville) [26, 27] which fall about 6 cm^3 mol^{-1} lower. The values cited are from a smooth curve through the upper data.

w A smooth curve was drawn by eye through all points found in [2] in the range 250 to 325 K. The points were found by interpolation on the curve.

x All values listed for B_{12} in [2] in the range 250 to 325 K were plotted and a smooth curve drawn by eye through the points. The data listed were obtained by interpolation on the curve.

y A curve was drawn through all values for B_{12} listed in [2] in the range 250 to 325 K. The data scatter badly. The curve was drawn with slightly greater slope than for propane and methane, but otherwise of a similar shape. The values listed were interpolated on the curve.

z Only one point is given for iso-butane plus methane. A curve was drawn through it and equally proportioned between the curves for methane plus propane and methane plus n-butane.

aa For n-pentane plus methane values of B_{12} scatter badly and the slopes from different sources are not consistent. A curve with minimum slope was drawn. The value at 273.15 K had to be extrapolated; otherwise points were interpolated.

bb Very bad scatter; a curve was drawn parallel to n-pentane, and a little less negative.

cc For 2,2-dimethylpropane plus methane the data of Strein [13], Hamann [34], and Belim [20] were plotted, a curve drawn through [13] and [20] fell about 25 cm^3 mol^{-1} more negative than for [34]. Other data by Baughman [35] from 199 to 257 K was plotted and values were less negative. Values were extrapolated from the curve drawn through data of [34].

dd For n-hexane plus methane the data of Pecsok [32] and Dantzler [29] were plotted and a smooth curve was drawn by eye and values extrapolated.

ee For 2,2-dimethylbutane plus methane a smooth curve was drawn by eye through the only two points given by Pecsok [32] and values were extrapolated.

ff A uniform uncertainty of ±100 cm^3 mol^{-1} is used for the hexanes on the basis of [2] and cyclohexane at 300 K. The uncertainty is probably larger at 273.15 K because of lack of data.

gg Ref. [2] does not list smoothed data below 300 K. The data point given at 298.15 K is from [4].

hh Uncertainty taken equal to that for CO_2-free dry air.

ii Uncertainty taken as twice that of helium.

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Table A9a. Constants for quadratic equations for the virial coefficients as functions of T in the range 273 to 300 K[a]

$$B = c + dT + eT^2$$

Substance	c / $cm^3\ mol^{-1}$	d / $cm^3\ mol^{-1}\ K^{-1}$	e / $10^{-3}\ cm^3\ mol^{-1}\ K^{-2}$
methane	-264.3	-1.0899	-1.166
ethane	-1333.6	-6.4626	-8.763
propane	-1618.0	-5.1270	-3.303
n-butane	-7937.1	+42.5325	-61.636
2-methylpropane	-18764.8	+117.552	-190.852
n-pentane	-25054.4	+148.949	-232.017
2-methylbutane	-10077.8	+52.7664	-75.838
2,2-dimethylpropane	-11735.3	+63.9039	-92.816
n-hexane	---	---	---
2-methlypentane	-3577.8	-1.8440	+27.174
3-methlypentane	-16491.6	+87.5927	-127.131
2,2-dimethylbutane	---	---	---
2,3-dimethylbutane	-15607.0	-85.6304	-128.881
ethyne	---	---	---
ethene	-912.2	+4.2046	-5.413
propene	-1577.5	+5.5834	-4.873
benzene	-17679.2	+97.4720	-144.782
carbon monoxide	---	---	---
carbon dioxide	-1280.8	+6.9745	-10.374
oxygen	-110.8	+0.4066	+0.299
nitrogen	-151.7	+0.7923	-1.009
helium	+2.0	+0.0773	-0.149
argon	-185.3	+0.9461	-1.271
hydrogen	+62.7	-0.3694	+0.696
air (CO_2-free, dry)	-154.7	+0.7924	-1.009
water vapor	---	---	---

[a]Data in Table 8 were fitted to the quadratic form. The main use is to obtain dB/dT near 288 K. Because some points are extrapolated, these expressions must be considered to be approximate.

Table A9b. Constants for quadratic equations for the second virial coefficients of interaction, $B(1,i)$, as functions of temperature for the range 273 to 300 K[a]

$$B(1,i) = c + dT + eT^2 \text{ (1 = methane)}$$

Substance pair	c / $cm^3\ mol^{-1}$	d / $cm^3\ mol^{-1}\ K^{-1}$	e / $10^{-3}\ cm^3\ mol^{-1}\ K^{-2}$
methane + ethane	-661.6	+3.2100	-4.358
(1)[b] + propane	-560.8	+2.0478	-2.044
(1) + n-butane	-899.5	+3.7585	-4.478
(1) + 2-methylpropane	-941.2	+4.3346	-5.627
(1) + n-pentane	-1276.3	+5.6426	-7.076
(1) + 2-methlybutane	-1449.9	+7.0162	-9.551
(1) + 2,2-dimethylpropane	-3123.8	+18.7127	-29.534
(1) + n-hexane	-3201.1	+18.7225	-29.901
(1) + 2-methylpentane	---	---	---
(1) + 3-methylpentane	---	---	---
(1) + 2,2-dimethlybutane	-4491.4	+26.2291	-39.888
(1) + 2,3-dimethlybutane	---	---	---
(1) + cyclopropane	---	---	---
(1) + cyclobutane	---	---	---
(1) + cyclopentane	---	---	---
(1) + cyclohexane	---	---	---
(1) + ethyne	---	---	---
(1) + ethene	-496.1	+2.2641	-2.738
(1) + propene	---	---	---
(1) + benzene	---	---	---
(1) + carbon monoxide	---	---	---
(1) + carbon dioxide	---	---	---
(1) + oxygen	---	---	---
(1) + nitrogen	-333.8	+2.0150	-3.198
(1) + helium	---	---	---
(1) + argon	-368.1	+2.0854	-3.090
(1) + hydrogen	+89.9	-0.7904	+1.769
(1) + air (CO_2-free, dry)	---	---	---
(1) + water vapor	-545.3	+2.4226	-2.700

[a]See footnote to Table A9a.

[b](1) = methane.

Table A9c. Enthalpy differences, $H - H^{\circ}$, between the real and ideal gases for pure substances p = 101.325 kPa at various reference temperatures

Substance	$\frac{H - H^{\circ}}{J \cdot mol^{-1}}$			
T/K	273.15	288.15	288.71	298.15
methane	-18.0	-17.0	-17.0	-16.3
ethyne	---	---	---	---
ethene	-51.9	-47.2	-47.0	-43.9
ethane	-69.6	-61.9	-61.6	-56.6
propene	-125.	-121.	-121.	-118.
propane	-142.	-139.	-139.	-136.
cyclobutane	---	---	---	---
n-butane	-353.	-296.	-294.	-257.
2-methlypropane	-478.	-306.	-299.	-188.
cyclopentane	---	---	---	---
n-pentane	-854.	-626.	-618.	-475.
2-methylbutane	-478.	-404.	-401.	-355.
2,2-dimethylpropane	-517.	-428.	-424.	-368.
benzene	-767.	-619.	-613.	-521.
cyclohexane	---	---	---	---
n-hexane	---	---	---	---
2-methylpentane	-633.	-647.	-647.	-657.
3-methylpentane	-790.	-656.	-651.	-568.
2,2-dimethylbutane	---	---	---	---
2,3-dimethylbutane	-667.	-537.	-532.	-451.
carbon monoxide	---	---	---	---
carbon dioxide	-51.7	-42.7	-42.4	-36.5
oxygen	-8.98	-8.72	-8.71	-8.54
nitrogen	-7.74	-6.88	-6.85	-6.28
helium	1.33	1.46	1.47	1.55
argon	-9.18	-8.09	-8.05	-7.33
hydrogen	1.09	0.50	0.48	0.09
air (CO_2 free dry)	-8.05	-7.19	-7.15	-6.59
water vapor	---	---	---	---

Appendix 10. Propagation of uncertainties

Propagation of uncertainties

In calculating the propagation of uncertainties, we use the relationship, below, recommended by the IUPAC Commission on Thermodynamics [17]*. Where a quantity F is a function of variables x,y,z:

$$F = F(x,y,z) \qquad (A10.1)$$

then the uncertainty s_F in F is related to the uncertainties in x, y, and z by the equation:

$$(s_F)^2 = (\partial F/\partial x)^2\ s_x^2 + (\partial F/\partial y)^2\ s_y{}^2 + (\partial F/\partial z)^2\ s_z^2 \qquad (A10.2)$$

Strictly speaking, x, y and z must be independent, non-correlated variables for this equation to hold. Usually, when there is some correlation this equation gives an upper limit. It is adopted here as an *ad hoc* expression to define the method of calculations.

In this document we use several functions of the type:

$$F = ax \qquad (A10.3)$$

$$F = ax + by - cz \qquad (A10.4)$$

where a, b, and c, are constants.

For equation (A10.3), by application of (A10.2) we obtain:

$$s_F^2 = \{\partial ax)/\partial x\}^2\ s_x^2 + \{\partial(ax)/\partial a\}^2\ s_a^2 \qquad (A10.5)$$

Since a is a constant $s_a = 0$ and the last term of (A10.5) is zero. As a result:

$$s_F^2 = a^2 s_x^2 = (as_x)^2 \qquad (A10.6)$$

or

$$s_F = as_x \qquad (A10.7)$$

---

*See general list of references.

For equation (A10.4), by application of (A10.2) we have, dropping the zero terms as above:

$$s_F^2 = \{\partial(ax)/\partial x\}^2\ s_x^2 + \{\partial(by)/\partial y\}^2\ s_y^2 + \{\partial(-cz)/\partial z\}^2\ s_z^2 \quad . \quad \text{(A10.8)}$$

This reduces to:

$$s_F^2 = a^2 s_x^2 + b^2 s_y^2 + (-c)^2 s_z^2 \quad \text{(A10.9)}$$

$$s_F^2 = (as_x)^2 + (bs_y)^2 + (cx_z)^2 \quad \text{(A10.10)}$$

or:

$$s_F = \{(as_x)^2 + (bs_y)^2 + (cs_z)^2\}^{\frac{1}{2}} \quad \text{(A10.11)}$$

Uncertainties in enthalpies of combustion and enthalpies of formation under different conditions

(a) Enthalpies of combustion and formation

The chemical equation for the combustion reaction:

$$C_aH_b + (a + b/4)O_2 = aCO_2 + (b/2)H_2O \quad \text{(A10.12)}$$

leads to relationships between the enthalpies of formation $\Delta_f H°$ and the enthalpy of combustion $\Delta_c H°$:

$$\Delta_c H°(C_aH_b) = a\Delta_f H°(CO_2) + (b/2)\ \Delta_f H°(H_2O) - (a+b/4)\ \Delta_f H°(O_2)$$
$$-\Delta_f H°(C_aH_b) \quad \text{(A10.13)}$$

which is a function of the type of equation (A10.4). By application of equation (A10.2) as illustrated in equations (A10.3 - 11) we obtain:

$$s_c(C_aH_b) = [\{as_f(CO_2)\}^2 + \{(b/2)s_f(H_2O)\}^2 +$$
$$+ \{(a + b/4)s_f(O_2)\}^2 + \{s_f(C_aH_b)\}^2]^{\frac{1}{2}} \quad , \quad \text{(A10.14)}$$

or alternatively:

$$s_f(C_aH_b) = [\{as_f(CO_2)\}^2 + \{(b/2)s_f(H_2O)\}^2$$
$$+ \{(a + b/4)s_f(O_2)\}^2 + \{s_c(C_aH_b)\}^2]^{\frac{1}{2}} \quad \text{(A10.15)}$$

depending on whether $\Delta_c H°(C_aH_b)$ or $\Delta_f H°(C_aH_b)$ is taken as the dependent quantity. In the above equation $\Delta_f H°(O_2) \equiv 0$ and $s_f(O_2) = 0$.

(b) Adjustment from one temperature to another

For the adjustment of heating values from one temperature to another, the following relationships are derived from equation (A10.12).

$$\Delta_c H^\circ_T(C_aH_b) = \Delta_c H^\circ_{298.15K}(C_aH_b)$$
$$+ a\{(H^\circ_T - H^\circ_{298.15\ K})(CO_2)\} + (b/2)\ \{(H^\circ_T - H^\circ_{298.15\ K})(H_2O,1)\}$$
$$- (a + b/4)\ \{(H^\circ_T - H^\circ_{298.15\ K})(O_2)\} - \{(H^\circ_T - H^\circ_{298.15\ K})(C_aH_b)\} \qquad \text{(A10.16)}$$

Equation (A10.16) is also a function of the type of equation (A10.4). From equation (16) we derive:

$$\{s_c(T)\}^2 = \{s_c(298.15\ K)\}^2 + \{as_{H(T)}(CO_2)\}^2 + \{(b/2)s_{H(T)}(H_2O,1)\}^2$$
$$+ \{(a + b/4)s_{H(T)}(O_2)\}^2 + \{s_{H(T)}(C_aH_b)\}^2\ , \qquad \text{(A10.17)}$$

in which $s_c(T)$ is the estimated uncertainty in enthalpy of combustion at T, $s_c(298.15\ K)$ is the estimated uncertainty in enthalpy of combustion at $T = 298.15$ K (Table A7g) and $s_{H(T)}$ is the estimated uncertainty in the quantity $(H^\circ_T - H^\circ_{298.15\ K})$ for the subtance identified parenthetically beside it.

Conversion of enthalpy from molar to mass basis

In calculating $\Delta_c H^\circ_w$ we use the relationship:

$$\Delta_c H^\circ_w = \Delta_c H^\circ_m/M \qquad \text{(A10.18)}$$

where M is the molar mass. From equation (A10.2) we have:

$$s^2_{cw} = \{\partial(\Delta_c H^\circ_w)/\partial(\Delta_c H^\circ_m)\}^2\ (s_{cm})^2 + \{\partial(\Delta_c H^\circ_w)/\partial M\}^2 (s_m)^2 \qquad \text{(A10.19)}$$

$$\partial(\Delta_c H^\circ_w)/\partial(\Delta_c H^\circ_m) = 1/M \qquad \text{(A10.19a)}$$

$$\partial(\Delta_c H^\circ_w)/\partial M = -\ \Delta_c H^\circ_m/M^2 \qquad \text{(A10.19b)}$$

s_{cm} for this purpose is s_c from Table A7g; s_M is found in the discussion on atomic weights in Section 13 and Appendix 5a.

$$s^2_{cw} = (1/M)^2(s_{cm})^2 + \{(\Delta_c H_m)/M^2\}^2\ (s_M)^2 \qquad \text{(A10.20)}$$

In equations (A10.20 and A10.20a), s_{cw} and s_{cm} are the estimated uncertainties of $\Delta_c H^\circ_w$ and $\Delta_c H^\circ_m$ respectively. s_M is the estimated uncertainty in the molar mass. We can obtain the estimated relative uncertainty $(s_{cw}/\Delta_c H^\circ_w)$ by dividing equation (A10.20) by $(\Delta_c H^\circ_w)^2 = (\Delta_c H^\circ_m/M)^2$. We thus obtain:

$$(s_{cw}/\Delta_c H^\circ_w)^2 = (s_{cm}/\Delta_c H^\circ_m)^2 + (s_M/M)^2 \qquad \text{(A10.20a)}$$

Conversion of enthalpies from molar to volumetric basis

(a) Uncertainty in ideal gas molar volume

In calculating V_m^{id} we use the relationship:

$$V_m^{id} = RT/p \qquad \text{(A10.21)}$$

In a manner similar to that used in earlier examples, we obtain:

$$\{s^{id}_{V(T,p)}/V^{id}_{T,p}\}^2 = (s_R/R)^2 + (s_T/T)^2 + (s_p/p)^2 \qquad \text{(A10.22)}$$

(b) Conversion of enthalpy

In calculating $\Delta_c H^\circ_v$ from $\Delta_c H^\circ_m$ we use the relationships:

$$\Delta_c H^\circ_v = \Delta_c H^\circ_m/V_m^{id} \qquad \text{(A10.23)}$$

$$(s^{id}_{cv}/\Delta_c H^\circ_v)^2 = (s^{id}_{cm}/\Delta_c H^\circ_m)^2 + (s^{id}_{V(T,p)}/V_m^{id})^2 \qquad \text{(A10.24)}$$

(c) Uncertainty in the ideal gas volume of water saturated gas

For the dry gas, the partial pressure of the fuel gas p for equation (A10.21) is equal to the defined reference pressure p°. However for the water saturated gas, V_m requires that $p(\text{fuel}) = p^\circ - p(H_2O)$ at that temperature. The uncertainty $s(p,\text{fuel})$ in the partial pressure of fuel is obtained from:

$$\{s(p,\text{fuel})\}^2 = \{s(p^\circ)\}^2 + \{s(p,H_2O)\}^2 \qquad \text{(A10.25)}$$

Because p° is a defined constant $s(p^\circ) = 0$ and:

$$\{s(p,\text{fuel})\}^2 = \{s(p,H_2O)\}^2 \qquad \text{(A10.26)}$$

for the water saturated gas.

Uncertainties of Virial Coefficients

The estimated uncertainties $s(B)$ in the virial coefficients B are given in Table 8a for pure substances and in Table 8b for binary interactions between substances. The uncertainty of the virial coefficient of a mixture is dependent on the composition of the mixture as is discussed below.

We start with the general function:

$$B(\text{mix}) = B(B_{ij}, x_i) \tag{A10.27}$$

in which B(mix) is the virial coefficient of the mixture having n individual components i or j, x_i is the mole fraction of component i and B_{ij} is the virial coefficient corresponding to binary interactions between molecules of i and of j. If j = i the virial coefficient is that of pure substance i.

If B(mix) has the functional form given in equation (A10.28) it can be shown by simple algebraic manipulation based on equation (A10.2) that the uncertainty s(B,mix) can be separated into two independent sets of contributing terms, equation (A10.29) below, one of which depends on the uncertainties $s(B_{ij})$ in the virial coefficients and the other depends on the uncertainties $s(x_i)$ in the composition.

$$\begin{aligned} B(\text{mix}) = {} & B_{11}x_1^2 + B_{22}x_2^2 + B_{33}x_3^2 + B_{44}x_4^2 + \ldots \\ & + 2B_{12}x_1x_2 + 2B_{13}x_1x_3 + 2B_{14}x_1x_4 + \ldots \\ & + 2B_{23}x_2x_3 + 2B_{24}x_2x_4 + \ldots \\ & + 2B_{34}x_3x_4 + \ldots \end{aligned} \tag{A10.28}$$

$$\{s(B,\text{mix})\}^2 = \sum_{ij} \{\partial B(\text{mix})/\partial B_{ij}\}^2 \{s(B_{ij})\}^2 + \sum_i \{\partial B(\text{mix})/\partial x_i\}^2 \{s(x_i)\}^2 \tag{A10.29}$$

Because the x_i are variables that are particular to a gas mixture and are measured parameters, except for illustrative purposes of defined gas mixtures, the assignment of $s(x_i)$ is dependent on the measurement process used, and is beyond the scope of this chapter. However the relationship of s(B,mix) to $s(x_i)$ can be shown.

The coefficients in the first set of terms on the right hand side of equation (A10.29) all have the form:

$$(\partial B(\text{mix})/\partial B_{ij}) = x_i x_j \tag{A10.30}$$

The coefficients in the second set of terms in equation (A10.29) are more complex because the x_i's are not all independent but must sum to unity:

$$\Sigma x_i = 1 \qquad \text{(A10.31)}$$

If this condition is ignored the coefficient of each $(s(x_i))^2{}_i$ is:

$$(\partial B(mix)/\partial x_i)^2 = (2\Sigma_j B_{ij}x_j)^2 \qquad j = 1,2,\ldots.n \qquad \text{(A10.32)}$$

When the condition A10.31 is introduced in equation A10.28 in the form:

$$x_1 = 1 - x_2 - x_3 - x_4 - \ldots \qquad \text{(A10.33)}$$

the coefficients of the $(s(x_i))^2$ are replaced by terms of the form shown in equations (A10.34) below.

$s(x_i)$	coefficient: $(\partial B(mix)/\partial x_i)^2$
$s(x_1)$	-
$s(x_2)$	$[2(B_{12}-B_{11}) + 2(B_{22}-2B_{12}+B_{11})x_2 + 2(B_{11}-B_{12}-B_{13}+B_{23})x_3 + 2(B_{11}-B_{12}-B_{14}+B_{24})x_4 + 2(B_{11}-B_{12}-B_{15}+B_{25})x_5 \ldots]^2$
$s(x_3)$	$[2(B_{13}-B_{11}) + 2(B_{11}-B_{12}-B_{13}+B_{23})x_2 + 2(B_{11}-2B_{13}+B_{33})x_3 + 2(B_{11}-B_{13}-B_{14}+B_{34})x_4 + 2(B_{11}-B_{13}-B_{15}+B_{35})x_5 + ..]^2$ (A10.34)
$s(x_4)$	$[2(B_{14}-B_{11}) + 2(B_{11}-B_{12}-B_{14}+B_{24})x_2 + 2(B_{11}-B_{13}-B_{14}+B_{34})x_3 + 2(B_{11}-2B_{14}+B_{44})x_4 + 2(B_{11}-B_{14}-B_{15}+B_{45})x_5 + ..]^2$
$s(x_5)$	.. ..

The final result, for the real gas mixture in which the errors in composition are constrained by the fact that $\Sigma\, x_i = 1$, is given by equation (A10.35).

$$
\begin{aligned}
\{s(B,\mathrm{mix})\}^2 = {} & (x_1^2)^2\{s(B_{11})\}^2 + (2x_1x_2)^2\ \{s(B_{12})\}^2 \\
& + (2x_1x_3)^2\ \{s(B_{13})\}^2 + (2x_1x_4)^2\ \{s(B_{14})\}^2 + .. \\
& + (x_2^2)^2\ \{s(B_{22})\}^2 + (2x_2x_3)^2\ \{s(B_{23})\}^2 + .. \\
& + (x_3^2)^2\ \{s(B_{33})\}^2 + (2x_3x_4)^2\ \{s(B_{34})\}^2 + .. \\
& + (x_4^2)^2\ \{s(B_{44})\}^2 + \ldots \\
& + \ldots \\
& + \{2(B_{12}-B_{11}) + 2(B_{22}-2B_{12}+B_{11})x_2 + 2(B_{11}-B_{12}-B_{13}+B_{23})x_3 \\
& + 2(B_{11}-B_{12}-B_{14}-B_{22})x_4 + \ldots]^2\ \{s(x_2)\}^2 \\
& + \{2(B_{13}-B_{11}) + 2(B_{11}-B_{12}-B_{13}+B_{23})x_2 + 2(B_{11}-2B_{13}+B_{33})x_3 \\
& + 2(B_{11}-B_{13}-B_{14}+B_{34})x_4 + \ldots]^2\ \{s(x_3)\}^2 \\
& + \{2(B_{14}-B_{11}) + 2(B_{11}-B_{12}-B_{14}+B_{24})x_2 + 2(B_{11}-B_{13}-B_{14}+B_{34})x_3 \\
& + 2(B_{11}-2B_{14}+B_{44})x_4 + \ldots]^2\ \{s(x_4)\}^2
\end{aligned}
\tag{A10.35}
$$

In practice, drastic simplification of the general result is required (by the lack of data) and is warranted (by the small size of many terms). Usually, for the coefficients of $s(B_{ij})$ only terms involving x_1 will be large enough to matter. The situation is less clear for the coefficients of $s(x_i)$ unless that quantity itself is very small, because (1), only mole fractions of the impurities appear, and, (2), some B_{ij} are likely to be unknown. In some cases the entire set of terms in $s(x_i)$ will be small, but each case must be tested.

Uncertainties in $\mathrm{d}B/\mathrm{d}T$

$B(T)$ is fitted by equation of type (A10.36) for which constants and their uncertainties are listed in Tables A9a and A9b.

$$B(T) = c + dT + eT^2 \tag{A10.36}$$

$$\mathrm{d}B/\mathrm{d}T = d + 2eT \tag{A10.37}$$

Using equation (A10.2) we calculated $s(dB/dT)$ as follows:

$$\{s(dB/dT)\}^2 = \{\partial[dB/dT)\partial b]^2 \{s(b)\}^2 + \{\partial(dB/dT)/\partial\}^2 \{s(c)\}^2 + \{\partial(dB/dT)/\partial T\}^2 \{s(T)\}^2 \quad . \tag{A10.38}$$

Because T is the independent variable, $s(T)$ will be taken as zero. We obtain:

$$\{s(dB/dT)\}^2 = \{2Ts(c)\}^2 \tag{A10.39}$$

NBS-114A (REV. 2-80)

U.S. DEPT. OF COMM. **BIBLIOGRAPHIC DATA SHEET** *(See instructions)*	1. PUBLICATION OR REPORT NO. NBSIR 81-2401	2. Performing Organ. Report No.	3. Publication Date

4. TITLE AND SUBTITLE

Heating Values of Natural Gas and its Components
Conversion of values to measurement bases and calculation of mixtures

5. AUTHOR(S)

George T. Armstrong and Thomas L. Jobe, Jr.

6. PERFORMING ORGANIZATION *(If joint or other than NBS, see instructions)*

NATIONAL BUREAU OF STANDARDS
DEPARTMENT OF COMMERCE
WASHINGTON, D.C. 20234

7. Contract/Grant No.

8. Type of Report & Period Covered

9. SPONSORING ORGANIZATION NAME AND COMPLETE ADDRESS *(Street, City, State, ZIP)*

Groupe Internationale des Importateurs de Gaz Natural Liquefie (GIIGNL)

10. SUPPLEMENTARY NOTES

☐ Document describes a computer program; SF-185, FIPS Software Summary, is attached.

11. ABSTRACT *(A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here)*

The standard enthalpies of combustion of the pure hydrocarbons C_1 to C_6 at 298.15 K and 101 325 Pa selected from the literature, with reference to a more detailed document, are used to derive heating values for the ideal gas and the real gas on molar, mass, and volumetric bases at five reference conditions involving other temperatures and pressures. Values can be obtained at both dry and water saturated conditions. The second virial coefficients and their first derivatives are used to calculate the effects of non-ideality. Procedures are given and illustrated for calculating the heating values of mixtures from the composition and the data given for the pure compounds. The relationships between the quantities presented in the tables are illustrated by charts. A procedure is given for estimating the uncertainties of the calculated results.

12. KEY WORDS *(Six to twelve entries; alphabetical order; capitalize only proper names; and separate key words by semicolons)*

Heating value; calorific value; enthalpy of combustion; hydrocarbon gases; gaseous fuel mixtures; real gas; ideal gas; estimation from composition; reference measurement conditions

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14. NO. OF PRINTED PAGES

164

15. Price

15.00