



Designation: D3588 – 98 (Reapproved 2017)

# Standard Practice for Calculating Heat Value, Compressibility Factor, and Relative Density of Gaseous Fuels<sup>1</sup>

This standard is issued under the fixed designation D3588; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

## 1. Scope

1.1 This practice covers procedures for calculating heating value, relative density, and compressibility factor at base conditions (14.696 psia and 60°F (15.6°C)) for natural gas mixtures from compositional analysis.<sup>2</sup> It applies to all common types of utility gaseous fuels, for example, dry natural gas, reformed gas, oil gas (both high and low Btu), propane-air, carbureted water gas, coke oven gas, and retort coal gas, for which suitable methods of analysis as described in Section 6 are available. Calculation procedures for other base conditions are given.

1.2 The values stated in inch-pound units are to be regarded as the standard. The SI units given in parentheses are for information only.

1.3 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

1.4 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

## 2. Referenced Documents

### 2.1 ASTM Standards:<sup>3</sup>

<sup>1</sup> This practice is under the jurisdiction of ASTM Committee D03 on Gaseous Fuels and is the direct responsibility of Subcommittee D03.03 on Determination of Heating Value and Relative Density of Gaseous Fuels.

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<sup>2</sup> A more rigorous calculation of  $Z(T,P)$  at both base conditions and higher pressures can be made using the calculation procedures in “Compressibility and Super Compressibility for Natural Gas and Other Hydrocarbon Gases,” American Gas Association Transmission Measurement Committee Report 8, AGA Cat. No. XQ1285, 1985, AGA, 1515 Wilson Blvd., Arlington, VA 22209.

<sup>3</sup> For referenced ASTM standards, visit the ASTM website, [www.astm.org](http://www.astm.org), or contact ASTM Customer Service at [service@astm.org](mailto:service@astm.org). For *Annual Book of ASTM Standards* volume information, refer to the standard’s Document Summary page on the ASTM website.

D1717 Test Method for Test for Analysis of Commercial Butane-Butene Mixtures and Isobutylene by Gas Chromatography (Withdrawn 1984)<sup>4</sup>

D1945 Test Method for Analysis of Natural Gas by Gas Chromatography

D1946 Practice for Analysis of Reformed Gas by Gas Chromatography

D2163 Test Method for Determination of Hydrocarbons in Liquefied Petroleum (LP) Gases and Propane/Propene Mixtures by Gas Chromatography

D2650 Test Method for Chemical Composition of Gases by Mass Spectrometry

### 2.2 GPA Standards:

GPA 2145 Physical Constants for the Paraffin Hydrocarbons and Other Components in Natural Gas<sup>5</sup>

GPA Standard 2166 Methods of Obtaining Natural Gas Samples for Analysis by Gas Chromatography<sup>5</sup>

GPA 2172 Calculation of Gross Heating Value, Relative Density, and Compressibility Factor for Natural Gas Mixtures from Compositional Analysis<sup>5,6</sup>

GPA Standard 2261 Method of Analysis for Natural Gas and Similar Gaseous Mixtures by Gas Chromatography<sup>5</sup>

GPA Technical Publication TP-17 Table of Physical Properties of Hydrocarbons for Extended Analysis of Natural Gases<sup>5</sup>

GPSA Data Book, Fig. 23-2, Physical Constants<sup>5</sup>

### 2.3 TRC Document:

TRC Thermodynamic Tables—Hydrocarbons<sup>7</sup>

<sup>4</sup> The last approved version of this historical standard is referenced on [www.astm.org](http://www.astm.org).

<sup>5</sup> Available from Gas Processors Association (GPA), 6526 E. 60th St., Tulsa, OK 74145, <http://www.gasprocessors.com>.

<sup>6</sup> The sole source of supply of the program in either BASIC or FORTRAN suitable for running on computers known to the committee at this time is the Gas Processors Association. If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee<sup>1</sup>, which you may attend.

<sup>7</sup> Available from Thermodynamics Research Center, The Texas A&M University, College Station, TX 77843-3111.

## 2.4 ANSI Standard:

**ANSI Z 132.1-1969: Base Conditions of Pressure and Temperature for the Volumetric Measurement of Natural Gas**<sup>8,9</sup>

## 3. Terminology

### 3.1 Definitions:

3.1.1 *British thermal unit*—the defined International Tables British thermal unit (Btu).

3.1.1.1 *Discussion*—The defining relationships are:

$$1 \text{ Btu} \cdot \text{lb}^{-1} = 2.326 \text{ J} \cdot \text{g}^{-1} \text{ (exact)}$$

$$1 \text{ lb} = 453.592 \text{ 37 g (exact)}$$

By these relationships, 1 Btu = 1 055.055 852 62 J (exact). For most purposes, the value (rounded) 1 Btu = 1055.056 J is adequate.

3.1.2 *compressibility factor* ( $z$ )—the ratio of the actual volume of a given mass of gas at a specified temperature and pressure to its volume calculated from the ideal gas law under the same conditions.

3.1.3 *gross heating value*—the amount of energy transferred as heat from the complete, ideal combustion of the gas with air, at standard temperature, in which all the water formed by the reaction condenses to liquid. The values for the pure gases appear in GPA Standard 2145, which is revised annually. If the gross heating value has a volumetric rather than a mass or molar basis, a base pressure must also be specified.

3.1.4 *net heating value*—the amount of energy transferred as heat from the total, ideal combustion of the gas at standard temperature in which all the water formed by the reaction remains in the vapor state. Condensation of any “spectator” water does not contribute to the net heating value. If the net heating value has a volumetric rather than a mass or molar basis, a base pressure must also be specified.

3.1.5 *relative density*—the ratio of the density of the gaseous fuel, under observed conditions of temperature and pressure, to the density of dry air (of normal carbon dioxide content) at the same temperature and pressure.

3.1.6 *standard cubic foot of gas*—the amount of gas that occupies 1 ft<sup>3</sup> (0.028 m<sup>3</sup>) at a temperature of 60°F (15.6°C) under a given base pressure and either saturated with water vapor (wet) or free of water vapor (dry) as specified (see ANSI Z 132.1). In this practice, calculations have been made at 14.696 psia and 60°F (15.6°C), because the yearly update of GPA 2145 by the Thermodynamics Research Center, on which these calculations are based, are given for this base pressure. Conversions to other base conditions should be made at the end of the calculation to reduce roundoff errors.

3.1.7 *standard temperature (USA)*—60°F (15.6°C).

### 3.2 Symbols:

#### 3.2.1 Nomenclature:

3.2.1.1  $B$ —second virial coefficient for gas mixture

3.2.1.2  $\sqrt{\beta_{ij}}$ —summation factor for calculating real gas correction (alternate method)

3.2.1.3 (cor)—corrected for water content

3.2.1.4 (dry)—value on water-free basis

3.2.1.5  $d$ —density for gas relative to the density of air.

3.2.1.6  $d^{id}$ —ideal relative density or relative molar mass, that is, molar mass of gas relative to molar mass of air

3.2.1.7  $G^{id}$ —molar mass ratio

3.2.1.8  $H_m^{id}$ —gross heating value per unit mass

3.2.1.9  $H_v^{id}$ —gross heating value per unit volume

3.2.1.10  $H_n^{id}$ —gross heating value per unit mole

3.2.1.11  $h_m^{id}$ —net heating value per unit mass

3.2.1.12  $h_v^{id}$ —net heating value per unit volume

3.2.1.13  $h_n^{id}$ —net heating value per unit mole

3.2.1.14 a, b, c—in Eq 1, integers required to balance the equation: C, carbon; H, hydrogen; S, sulfur; O, oxygen

3.2.1.15 (*id*)—ideal gas state

3.2.1.16 (*l*)—liquid phase

3.2.1.17  $M$ —molar mass

3.2.1.18  $m$ —mass flow rate

3.2.1.19  $n$ —number of components

3.2.1.20  $P$ —pressure in absolute units (psia)

3.2.1.21  $Q^{id}$ —ideal energy per unit time released as heat upon combustion

3.2.1.22  $R$ —gas constant, 10.7316 psia.ft<sup>3</sup>/(lb mol•R) in this practice (based upon  $R = 8.314 \text{ 48 J}/(\text{mol} \cdot \text{K})$ )

3.2.1.23 (sat)—denotes saturation value

3.2.1.24  $T$ —absolute temperature, °R = °F + 459.67 or  $K = °C + 273.15$

3.2.1.25 ( $T, P$ )—value dependent upon temperature and pressure

3.2.1.26  $V$ —gas volumetric flow rate

3.2.1.27  $x$ —mole fraction

3.2.1.28  $Z$ —gas compressibility factor repeatability of property

3.2.1.29  $\delta$ —repeatability of property

3.2.1.30  $\rho$ —density in mass per unit volume

3.2.1.31  $\sum_{j=1}^n$ —property summed for Components 1 through  $n$ , where  $n$  represents the total number of components in the mixture

### 3.2.2 Superscripts:

3.2.2.1 *id*—ideal gas value

3.2.2.2 *l*—liquid

3.2.2.3  $\sigma$ —value at saturation (vapor pressure)

3.2.2.4 '—reproducibility

### 3.2.3 Subscripts:

3.2.3.1  $a$ —value for air

3.2.3.2  $a$ —relative number of atoms of carbon in Eq 1

3.2.3.3  $b$ —relative number of atoms of hydrogen in Eq 1

3.2.3.4  $c$ —relative number of atoms of sulfur in Eq 1

3.2.3.5  $j$ —property for component  $j$

3.2.3.6  $ii$ —non-ideal gas property for component  $i$

3.2.3.7  $ij$ —non-ideal gas property for mixture of  $i$  and  $j$

3.2.3.8  $jj$ —non-ideal gas property for component  $j$

3.2.3.9  $w$ —value for water

<sup>8</sup> Available from American National Standards Institute (ANSI), 25 W. 43rd St., 4th Floor, New York, NY 10036, <http://www.ansi.org>.

<sup>9</sup> Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D03-1007.

3.2.3.10 1—property for Component 1

3.2.3.11 2—property for Component 2

#### 4. Summary of Practice

4.1 The ideal gas heating value and ideal gas relative density at base conditions (14.696 psia and 60°F (5.6°C)) are calculated from the molar composition and the respective ideal gas values for the components; these values are then adjusted by means of a calculated compressibility factor.

#### 5. Significance and Use

5.1 The heating value is a measure of the suitability of a pure gas or a gas mixture for use as a fuel; it indicates the amount of energy that can be obtained as heat by burning a unit of gas. For use as heating agents, the relative merits of gases from different sources and having different compositions can be compared readily on the basis of their heating values. Therefore, the heating value is used as a parameter for determining the price of gas in custody transfer. It is also an essential factor in calculating the efficiencies of energy conversion devices such as gas-fired turbines. The heating values of a gas depend not only upon the temperature and pressure, but also upon the degree of saturation with water vapor. However, some calorimetric methods for measuring heating values are based upon the gas being saturated with water at the specified conditions.

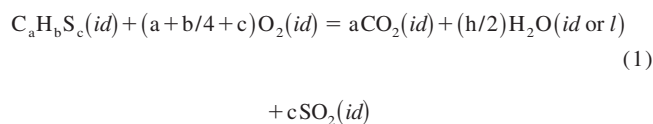
5.2 The relative density (specific gravity) of a gas quantifies the density of the gas as compared with that of air under the same conditions.

#### 6. Methods of Analysis

6.1 Determine the molar composition of the gas in accordance with any ASTM or GPA method that yields the complete composition, exclusive of water, but including all other components present in amounts of 0.1 % or more, in terms of components or groups of components listed in **Table 1**. At least 98 % of the sample must be reported as individual components (that is, not more than a total of 2 % reported as groups of components such as butanes, pentanes, hexanes, butenes, and so forth). Any group used must be one of those listed in **Table 1** for which average values appear. The following test methods are applicable to this practice when appropriate for the sample under test: Test Methods **D1717**, **D1945**, **D2163**, and **D2650**.

#### 7. Calculation—Ideal Gas Values; Ideal Heating Value

7.1 An ideal combustion reaction in general terms for fuel and air in the ideal gas state is:



where *id* denotes the ideal gas state and *l* denotes liquid phase. The ideal net heating value results when all the water remains in the ideal gas state. The ideal gross heating value results when all the water formed by the reaction condenses to liquid. For water, the reduction from  $H_2O(id)$  to  $H_2O(l)$  is  $H_w^{id} - H_w^l$ , the ideal enthalpy of vaporization, which is somewhat

larger than the enthalpy of vaporization  $H_w^y - H_w^l$ .

7.1.1 Because the gross heating value results from an ideal combustion reaction, ideal gas relationships apply. The ideal gross heating value per unit mass for a mixture,  $H_m^{id}$ , is:

$$H_m^{id} = \sum_{j=1}^n x_j M_j H_{m,j}^{id} / \sum_{j=1}^n x_j M_j \quad (2)$$

where:  $x_j$  is the mole fraction of Component *j*,  $M_j$  is the molar mass of Component *j* from **Table 1**, and *n* is the total number of components.

7.1.2  $H_{m,j}^{id}$  is the pure component, ideal gross heating value per unit mass for Component *j* (at 60°F (15.6°C) in **Table 1**). Values of  $H_m^{id}$  are independent of pressure, but they vary with temperature.

#### 7.2 Ideal Gas Density

7.2.1 The ideal gas density,  $\rho^{id}$ , is:

$$\rho^{id} = (P/RT) \sum_{j=1}^n x_j M_j = MP/RT \quad (3)$$

where: *M* is the molar mass of the mixture,

$$M = \sum_{j=1}^n x_j M_j \quad (4)$$

*P* is the base pressure in absolute units (psia), *R* is the gas constant, 10.7316 psia.ft<sup>3</sup>/(lb mol•°R) in this practice, based upon  $R = 8.31448 \text{ J}/(\text{mol}\cdot\text{K})$ , *T* is the base temperature in absolute units ( $^{\circ}\text{R} = ^{\circ}\text{F} + 459.67$ ). Values of the ideal gas density at 60°F (15.6°C) and 14.696 psia are in GPA Standard 2145.

#### 7.3 Ideal Relative Density:

7.3.1 The ideal relative density  $d^{id}$  is:

$$d^{id} = \sum_{j=1}^n x_j d_j = \sum_{j=1}^n x_j M_j / M_a = M / M_a \quad (5)$$

where:  $M_a$  is the molar mass of air. The ideal relative density is the molar mass ratio.

#### 7.4 Gross Heating Value per Unit Volume:

7.4.1 Multiplication of the gross heating value per unit mass by the ideal gas density provides the gross heating value per unit volume,  $H_v^{id}$ :

$$H_v^{id} = \rho^{id} H_m^{id} = \sum_{j=1}^n x_j H_{v,j}^{id} \quad (6)$$

$H_{v,j}^{id}$  is the pure component gross heating value per unit volume for Component *j* at specified temperature and pressure (60°F (15.6°C) and 14.696 psia in **Table 1**, ideal gas values).

7.4.2 Conversion of values in **Table 1** to different pressure bases results from multiplying by the pressure ratio:

$$H_v^{id}(P) = H_v^{id}(P = 14.696) \times P/14.696 \quad (7)$$

#### 7.5 Real Gas Values—Compressibility Factor:

7.5.1 The compressibility factor is:

$$Z(T,P) = \rho^{id} / \rho = (MP/RT) / \rho \quad (8)$$

where  $\rho$  is the real gas density in mass per unit volume. At conditions near ambient, the truncated virial equation of state satisfactorily represents the volumetric behavior of natural gas:

**TABLE 1 Properties of Natural Gas Components at 60°F and 14.696 psia<sup>A</sup>**

Compound	Formula	Molar Mass, lb·lbmol <sup>-1B</sup>	Molar Mass, Ratio, G <sup>dc</sup>	Ideal Gross Heating Value <sup>D</sup>			Ideal Net Heating Value			Summation Factor, b <sub>p</sub> , psia <sup>-1</sup>
				H <sub>v</sub> <sup>id</sup> , kJ·mol <sup>-1</sup>	H <sub>v</sub> <sup>id</sup> , Btu·lbm <sup>-1</sup>	H <sub>v</sub> <sup>id</sup> , Btu·ft <sup>-3</sup>	h <sub>v</sub> <sup>id</sup> , kJ·mol <sup>-1</sup>	h <sub>v</sub> <sup>id</sup> , Btu·lbm <sup>-1</sup>	h <sub>v</sub> <sup>id</sup> , Btu·ft <sup>-3</sup>	
Hydrogen	H <sub>2</sub>	2.0159	0.069 60	286.20	6 1022	324.2	241.79	51 566	273.93	0
Helium	He	4.0026	0.138 20	0	0	0	0	0	0	0
Water	H <sub>2</sub> O	18.0153	0.622 02	44.409	1059.8	50.312	0	0	0	0.0623
Carbon monoxide	CO	28.010	0.967 11	282.9	4342	320.5	282.9	4 342	320.5	0.0053
Nitrogen	N <sub>2</sub>	28.0134	0.967 23	0	0	0	0	0	0	0.0044
Oxygen	O <sub>2</sub>	31.9988	1.104 8	0	0	0	0	0	0	0.0073
Hydrogen sulfide	H <sub>2</sub> S	34.08	1.176 7	562.4	7 094.2	637.1	517.99	6 534	586.8	0.0253
Argon	Ar	39.948	1.379 3	0	0	0	0	0	0	0.0071
Carbon dioxide	CO <sub>2</sub>	44.010	1.519 6	0	0	0	0	0	0	0.0197
Air	<sup>E</sup>	28.9625	1.000 0	0	0	0	0	0	0	0.0050
Methane	CH <sub>4</sub>	16.043	0.553 92	891.63	23 891	1010.0	802.71	21 511	909.4	0.0116
Ethane	C <sub>2</sub> H <sub>6</sub>	30.070	1.038 2	1562.06	22 333	1769.7	1428.83	20 429	1618.7	0.0239
Propane	C <sub>3</sub> H <sub>8</sub>	44.097	1.522 6	2220.99	21 653	2516.1	2043.3	19 922	2314.9	0.0344
<i>i</i> -Butane	C <sub>4</sub> H <sub>10</sub>	58.123	2.006 8	2870.45	21 232	3251.9	2648.4	19 590	3000.4	0.0458
<i>n</i> -Butane	C <sub>4</sub> H <sub>10</sub>	58.123	2.006 8	2879.63	21 300	3262.3	2657.6	19 658	3010.8	0.0478
<i>i</i> -Pentane	C <sub>5</sub> H <sub>12</sub>	72.150	2.491 2	3531.5	21 043	4000.9	3265.0	19 456	3699.0	0.0581
<i>n</i> -Pentane	C <sub>5</sub> H <sub>12</sub>	72.150	2.491 2	3535.8	21 085	4008.9	3269.3	19 481	3703.9	0.0631
<i>n</i> -Hexane	C <sub>6</sub> H <sub>14</sub>	86.177	2.975 5	4198.1	20 943	4755.9	3887.2	19 393	4403.9	0.0802
<i>n</i> -Heptane	C <sub>7</sub> H <sub>16</sub>	100.204	3.459 8	4857.2	20 839	5502.5	4501.9	19 315	5100.3	0.0944
<i>n</i> -Octane	C <sub>8</sub> H <sub>18</sub>	114.231	3.944 1	5515.9	20 759	6248.9	5116.2	19 256	5796.2	0.1137
<i>n</i> -Nonane	C <sub>9</sub> H <sub>20</sub>	128.258	4.428 4	6175.9	20 701	6996.5	5731.8	19 213	6493.6	0.1331
<i>n</i> -Decane	C <sub>10</sub> H <sub>22</sub>	142.285	4.912 7	6834.9	20 651	7742.9	6346.4	19 176	7189.9	0.1538
Neopentane	C <sub>5</sub> H <sub>12</sub>	72.015	2.491 2	3517.27	20 958	3985	3250.8	19 371	3683	
2-Methylpentane	C <sub>6</sub> H <sub>14</sub>	86.177	2.975 5	4190.43	20 905	4747	3879.6	19 355	4395	0.080
3-Methylpentane	C <sub>6</sub> H <sub>14</sub>	86.177	2.975 5	4193.03	20 918	4750	3882.2	19 367	4398	0.080
2,2-Dimethylbutane	C <sub>6</sub> H <sub>14</sub>	86.177	2.975 5	4180.63	20 856	4736	3869.8	19 306	4384	0.080
2,3-Dimethylbutane	C <sub>6</sub> H <sub>14</sub>	86.177	2.975 5	4188.41	20 895	4745	3877.5	19 344	4393	0.080
Cyclopropane	C <sub>3</sub> H <sub>6</sub>	42.081	1.452 9	2092.78	21 381	2371	1959.6	20 020	2220	...
Cyclobutane	C <sub>4</sub> H <sub>8</sub>	56.108	1.937 3	2747.08	21 049	2747	2569.4	19 688	2911	...
Cyclopentane	C <sub>5</sub> H <sub>10</sub>	70.134	2.421 5	3322.04	20 364	3764	3100.0	19 003	3512	...
Cyclohexane	C <sub>6</sub> H <sub>12</sub>	84.161	2.905 9	3955.84	20 208	4482	3689.4	18 847	4180	...
Ethyne (acetylene)	C <sub>2</sub> H <sub>2</sub>	26.038	0.899 0	1301.32	21 487	1474	1256.9	20 753	1424	0.021
Ethene (ethylene)	C <sub>2</sub> H <sub>4</sub>	28.054	0.968 6	1412.06	21 640	1600	1323.2	20 278	1499	0.020
Propene (propylene)	C <sub>3</sub> H <sub>6</sub>	42.081	1.452 9	2059.35	21 039	2333	1926.1	19 678	2182	0.033
Benzene	C <sub>6</sub> H <sub>6</sub>	78.114	2.697 1	3202.74	18 177	3742	3169.5	17 444	3591	0.069
Butanes (ave)	C <sub>4</sub> H <sub>10</sub>	58.123	2.006 8	2875	21 266	3257	2653	19 623	3006	0.046
Pentanes (ave)	C <sub>5</sub> H <sub>12</sub>	72.150	2.491 2	3534	21 056	4003	3267	19 469	3702	0.062
Hexanes (ave)	C <sub>6</sub> H <sub>14</sub>	86.177	2.975 5	4190	20 904	4747	3879	19 353	4395	0.080
Butenes (ave)	C <sub>4</sub> H <sub>8</sub>	56.108	1.937 2	2716	20 811	3077	2538	19 450	2876	0.046
Pentenes (ave)	C <sub>5</sub> H <sub>10</sub>	70.134	2.421 5	3375	20 691	3824	3153	19 328	3572	0.060

<sup>A</sup> This table is consistent with GPA 2145-89, but it is necessary to use the values from the most recent edition of GPA 2145 for custody transfer calculations.  
<sup>B</sup> 1984 Atomic Weights: C = 12.011, H = 1.00794, O = 15.9994, N = 14.0067, S = 32.06.  
<sup>C</sup> Molar mass ratio is the ratio of the molar mass of the gas to that of air.  
<sup>D</sup> Based upon ideal reaction; the entry for water represents the total enthalpy of vaporization.  
<sup>E</sup> Composition from: F. E. Jones, *J. Res. Nat. Bur. Stand.*, Vol. 83, 419, 1978.

$$Z(T,P) = 1 + BP/RT \quad (9)$$

where *B* is the second virial coefficient for the gas mixture. The second virial coefficient for a mixture is:

$$B = x_1^2 B_{11} + x_2^2 B_{22} + \dots + x_n^2 B_{nn} + 2x_1x_2B_{12} + \dots + 2x_{n-1}x_nB_{n-1,n} \quad (10)$$

$$= \sum_{i=1}^n \sum_{j=1}^n x_i x_j B_{ij}$$

where *B<sub>ij</sub>* is the second virial coefficient for Component *j* and *B<sub>ij</sub>* is the second cross virial coefficient for Components *i* and *j*. The second virial coefficients are functions of temperature. Eq 9 can be used with Eq 10 for calculation of the compressibility factor for the various pressure bases, but it is not accurate at

pressures greater than two atmospheres. Special treatment is not required for H<sub>2</sub> and He at mole fractions up to 0.01. Calculations can be made with *B<sub>ij</sub>* = 0 for hydrogen and helium.

7.5.2 Eq 9 and Eq 10 for calculation of *Z(T,P)* for a gas mixture are rigorous but require considerable calculations and information that is not always available. An alternative, approximate expression for *Z(T,P)* that is more convenient for hand calculations is:

$$Z(T,P) = 1 - P \left[ \sum_{j=1}^n x_j \sqrt{\beta_{jj}} \right]^2 \quad (11)$$

where  $\beta_{jj} = B_{jj}/RT$  and  $\sqrt{\beta_{jj}}$  is the summation factor for

Component *j*. Values of  $\sqrt{\beta_{jj}}$  at 60°F (15.6°C) appear in **Table 2**. The method based upon **Eq 11** has been adopted for this practice.

**7.6 Real Gas Density:**

7.6.1 The real gas density  $\rho$  at a specific temperature and pressure is:

$$\rho = \rho^{id}/Z \tag{12}$$

where:  $\rho^{id}$  and *Z* are evaluated at the same temperature and pressure.

**7.7 Real Relative Density:**

7.7.1 The real relative density *d* is:

$$d = \rho/\rho_a = MZ_a/M_aZ \tag{13}$$

7.8 **Real Heating Value**—The real heating value is not given by division of the ideal heating value by the compressibility factor. Real gas heating values differ from the ideal gas values by less than one part in 10<sup>4</sup> at 14.696 psia, which is of the order of the accuracy of the heating values.

**7.9 Gross Heating Value of Water Wet Gas:**

7.9.1 If the gas contains water as a component but the compositional analysis is on a dry basis, it is necessary to adjust the mole fractions to reflect the presence of water. The corrected mole fractions are:

$$x_j(\text{cor}) = x_j(1 - x_w) \tag{14}$$

The mole fraction of water can range from zero up to the saturated value. The saturated value for  $x_w$  is, assuming Raoult's Law:

$$x_w(\text{sat}) = P_w^\circ/P \tag{15}$$

where:  $P_w^\circ$  is the vapor pressure of water (0.256 36 psia at 60°F (15.6°C)).

7.9.2 Technically, water has a gross heating value, the ideal enthalpy of condensation. If only the water that is formed during the combustion condenses, then the heat released upon combustion of a wet gas with dry air becomes:

$$H^{id}(\text{wet gas}) = (1 - x_w)H^{id}(\text{dry gas}) \tag{16}$$

For water-saturated gas,  $x_w$  at 60° F (15.6° C) is 0.256 36/ $P_b$ , where  $P_b$  is the base pressure. **Eq 16** is adequate for custody transfer applications as a matter of definition. However, this equation does not accurately describe the effect of water upon the heating value. **Appendix X1** contains a rigorous examination of the effect of water.

**7.10 Calculation of the Ideal Energy Released as Heat:**

7.10.1 When multiplied by the gas flow rate, the ideal gross heating value provides the ideal energy released as heat upon combustion,  $\dot{Q}^{id}$ , an ideal gas property:

$$\dot{Q}^{id} = \dot{m}H_m^{id} \tag{17}$$

where  $\dot{m}$  is the mass flow rate. For an ideal gas, the mass flow rate is related to the volumetric flow rate,  $\dot{V}^{id}$ , by:

$$\dot{m} = \dot{V}^{id} \rho^{id} \tag{18}$$

and

$$\dot{Q}^{id} = \dot{V}^{id}H_v^{id} \tag{19}$$

**TABLE 2 Example Calculations of Gas Properties at 60°F and 14.696 psia (Gas Analysis on Dry Basis)<sup>A</sup>**

NOTE 1—Division of  $H_v^{id}$  by *Z* does not give a real gas heating value but rather an ideal gas heating value per real cubic feet. Any digits carried beyond 1 part in 1000 are not significant but only alleviate roundoff error. Although CO<sub>2</sub> has a carbon atom, its  $\alpha = 0$  because it is not part of the fuel formula  $C_aH_bS_\gamma$ .

Compound	$x_i$	$\alpha_i$	$\beta_i$	$\gamma_i$	$Hv_i^{id}$	$G_i^{id}$	$b_i$	$x_i\mu_i$	$x_i\beta_i$	$x_i\gamma_i$	$x_iHv_i^{id}$	$x_iG_i^{id}$	$x_i b_i$
Methane	0.8302	1	4	0	1010.0	0.553 92	0.0116	0.8302	3.3208	0	838.5	0.4599	0.009 63
Ethane	0.0745	2	6	0	1769.7	1.038 20	0.0239	0.1490	0.4470	0	131.8	0.0773	0.001 78
Propane	0.0439	3	8	0	2516.1	1.522 60	0.0344	0.1317	0.3512	0	110.5	0.0668	0.001 51
<i>i</i> -Butane	0.0083	4	10	0	3251.9	2.006 80	0.0458	0.0332	0.0830	0	27.0	0.0167	0.000 38
<i>n</i> -Butane	0.0108	4	10	0	3262.3	2.006 80	0.0478	0.0432	0.1080	0	35.2	0.0217	0.000 52
<i>i</i> -Pentane	0.0031	5	12	0	4000.9	2.491 20	0.0581	0.0155	0.0372	0	12.4	0.0077	0.000 18
<i>n</i> -Pentane	0.0025	5	12	0	4008.9	2.491 20	0.0631	0.0125	0.03	0	10.0	0.0062	0.000 16
Hexane	0.0030	6	14	0	4755.9	2.975 50	0.0802	0.0180	0.0420	0	14.3	0.0089	0.000 24
Helium	0.0003	0	0	0	0	0.138 20	0	0	0	0	0	0.0000	0.000 00
Nitrogen	0.0032	0	0	0	0	0.967 23	0.0044	0	0	0	0	0.0031	0.000 01
Carbon dioxide	0.0202	0	0	0	0	1.519 60	0.0197	0	0	0	0	0.0307	0.000 40
Summation	1.0000	...	...	...	...	...	...	1.2333	4.4192	0	1179.7	0.6991	0.014 81

<sup>A</sup> $x_w = (0.256\ 36)/14.696 = 0.0174$   
 $G^{id}(\text{dry gas}) = 0.6991$   
 $Z(\text{dry gas}) = 1 - [0.014\ 81]^2(14.696) = 0.9968$   
 $Z(\text{dry air}) = 1 - [0.0050]^2(14.696) = 0.9996$   
 $G(\text{dry gas, dry air}) = 0.6991(0.9996)/0.9968 = 0.7011$   
 $G(\text{dry gas, sat air}) = 0.6991(0.9995)/0.9968 = 0.7010$   
 $Hv^{id}(\text{dry gas, dry air}) = 1179.7\ \text{Btu}\cdot\text{ft}^{-3}$   
 $Hv^{id}(\text{sat gas, dry air}) = 1179.7(0.9826) = 1159.1\ \text{Btu}\cdot\text{ft}^{-3}$   
 $1 - x_w = 0.9826$   
 $G^{id}(\text{sat gas}) = 0.6991(0.9826) + 0.0174(0.622\ 02) = 0.6978$   
 $Z(\text{sat gas}) = 1 - [0.9826(0.014\ 81) + 0.0174(0.0623)]^2(14.696) = 0.9964$   
 $Z(\text{sat air}) = 1 - [0.9826(0.0050) + 0.0174(0.0623)]^2(14.696) = 0.9995$   
 $G(\text{sat gas, dry air}) = 0.6978(0.9996)/0.9964 = 0.7001$   
 $G(\text{sat gas, sat air}) = 0.6978(0.9995)/0.9964 = 0.7000$   
 $\{Hv^{id}/Z\}(\text{dry gas, dry air}) = 1179.7/0.9968 = 1183.5\ \text{Btu}\cdot\text{ft}^{-3}$   
 $\{Hv^{id}/Z\}(\text{sat gas, dry air}) = 1159.1/(0.9964) = 1163.3\ \text{Btu}\cdot\text{ft}^{-3}$

7.10.2 The ideal gas flow rate is related to the real gas flow rate by:

$$\dot{V}^{id} = \dot{V}/Z \quad (20)$$

where  $\dot{V}$  is the real gas volumetric flow rate and  $Z(T,P)$  is the real gas compressibility factor at the same  $T$  and  $P$ . Hence, combining Eq 20 and Eq 21 gives:

$$\dot{Q}^{id} = H_v^{id} \dot{V}/Z(T,P) \quad (21)$$

NOTE 1—The ideal energy released per unit time as heat upon combustion,  $\dot{Q}^{id}$ , can be calculated using the mass flow rate (Eq 18), the ideal gas flow rate (Eq 20), or the real gas flow rate (Eq 22), but is always an ideal gas property. Division of  $H_v^{id}$  by the gas compressibility factor  $Z(T,P)$  does not produce a real gas heating value but only allows calculation of  $\dot{Q}^{id}$  using the real gas flow rate rather than the ideal gas flow rate.

### 8. Precision

8.1 The properties reported in this practice derive from experimental enthalpy of combustion measurements which, in general, are accurate to 1 part in 1000. The extra digits that appear in the accompanying tables alleviate problems associated with roundoff errors and internal consistency, but they are not significant. See Table 3.

8.2 The values of properties in this practice are those that appear in GPA Standard 2172-97, Fig. 23-2 of the GPSA Engineering Data Book, GPA TP-17, and the TRC Thermodynamic Tables—Hydrocarbons. GPA Standard 2145 is updated annually and the values in that standard should be used in all calculations.

NOTE 2—Three sources of error must be considered: errors in heating values of the components, errors in the calculated compressibility factor, and errors in the composition. The uncertainty (twice the standard deviation) of the ideal gas heating values for components should be 0.03 %. Such errors affect the bias and the agreement between calculated and measured heating values, but they do not affect the precision. Error in

the calculated compressibility factor varies with the composition of the gas, but for natural gas, this error should be less than 0.03 % and negligible compared to errors arising from uncertainty in composition. In this practice, the errors in the heating values of the components and the calculated compressibility factor,  $Z$ , are neglected. The precision of the method is related to the repeatability and reproducibility of the analysis. An example appears in .

NOTE 3—It is essential to include all components in the gas sample that appear with mole fractions greater than or equal to 0.001 in the analysis. Some routine analyses do not determine compounds such as He and H<sub>2</sub>S, but these compounds are important to the calculations.

### 8.3 Repeatability:

8.3.1 If all the components are analyzed and the results are normalized, then the repeatability of the heating value,  $\delta H$  is:

$$\frac{\delta H}{H^{id}} = \sqrt{\frac{1}{(H^{id})^2} \sum_{j=1}^n [(H^{id} - H_j^{id})\delta x_j]^2} \quad (22)$$

8.3.2 If the results of the analysis are made to sum to 1.0 by calculating the methane mole fraction as the difference between 1.0 and the sum of the mole fractions of the other components, then

$$\frac{\delta H}{H^{id}} = \sqrt{\frac{1}{(H^{id})^2} \sum_{j=1}^n [H_j^{id}\delta x_j]^2} \quad (23)$$

where  $\delta x_j$  is the repeatability of the method of analysis for Component  $j$ . The differences between heating values calculated from successive pairs of analysis performed by the same operator using the same sample of gas and the same instrument should exceed  $2\delta H$  in only 5 % of the tests when  $\delta H$  is taken as one standard deviation.

8.4 Reproducibility—The reproducibility  $\delta H'$  is calculated from Eq 25 and Eq 26 using  $\delta x'_j$ , the reproducibility of the method of analysis for Compound  $j$ . The difference between heating values calculated from analysis obtained in different laboratories is expected to exceed  $\delta H'$  for only 5 % of the analyses.

**TABLE 3 Example Calculations of Gas Properties at 60°F and 14.696 psia (Gas Analysis on Wet Basis)<sup>A</sup>**

NOTE 1—Division of  $H_v^{id}$  by  $Z$  does not give a real gas heating value but rather an ideal gas heating value per real cubic feet. Any digits carried beyond 1 part in 1000 are not significant but only alleviate roundoff error. Although CO<sub>2</sub> has a carbon atom, its  $\alpha = 0$  because it is not part of the fuel formula  $C_\alpha H_\beta S_\gamma$ .

Compound	$x_j$	$\alpha_j$	$\beta_j$	$\gamma_j$	$H_v^{id}$	$G_j^{id}$	$b_j$	$x_j\alpha_j$	$x_j\beta_j$	$x_j\gamma_j$	$x_j H_v^{id}$	$x_j G_j^{id}$	$x_j b_j$
Methane	0.8157	1	4	0	1010.0	0.553 92	0.0116	0.8157	3.2629	0	823.9	0.4518	0.009 46
Ethane	0.0732	2	6	0	1769.7	1.038 20	0.0239	0.1464	0.4392	0	129.5	0.0760	0.001 75
Propane	0.0431	3	8	0	2516.1	1.522 60	0.0344	0.1294	0.3451	0	108.5	0.0657	0.001 48
<i>i</i> -Butane	0.0082	4	10	0	3251.9	2.006 80	0.0458	0.0326	0.0816	0	26.5	0.0164	0.000 37
<i>n</i> -Butane	0.0106	4	10	0	3262.3	2.006 80	0.0478	0.0424	0.1061	0	34.6	0.0213	0.000 51
<i>i</i> -Pentane	0.0030	5	12	0	4000.9	2.491 20	0.0581	0.0152	0.0366	0	12.2	0.0076	0.000 18
<i>n</i> -Pentane	0.0025	5	12	0	4008.9	2.491 20	0.0631	0.0123	0.0295	0	9.8	0.0061	0.000 15
Hexane	0.0029	6	14	0	4755.9	2.975 50	0.0802	0.0177	0.0413	0	14.0	0.0088	0.000 24
Helium	0.0003	0	0	0	0	0.138 20	0	0	0	0	0	0	0
Nitrogen	0.0031	0	0	0	0	0.967 23	0.0044	0	0	0	0	0.0030	0
Carbon dioxide	0.0198	0	0	0	0	1.519 60	0.0197	0	0	0	0	0.0302	0.000 39
Water	0.0174	0	0	0	50.3	0.622 02	0.0623	0	0	0	0.9	0.0108	0.001 09
Summation	1.0000	...	...	...	...	...	...	1.2118	4.3421	0	1160.0	0.6977	0.015 64

<sup>A</sup> $G^{id}$  (sat gas) = 0.6977  
 $Z$  (sat gas) = 1 - [0.015 64]<sup>2</sup>(14.696) = 0.9964  
 $Z$  (dry air) = 1 - [0.0050]<sup>2</sup>(14.696) = 0.9996  
 $G$  (sat gas, dry air) = 0.6977(0.9996)/0.9964 = 0.6999  
 $H_v^{id}$  (sat gas, dry air) = 1160.0 - 0.9 = 1159.1 Btu-ft<sup>-3</sup>  
 $Z$  (sat air) = 1 - [0.9826(0.050) + 0.0174(0.0623)]<sup>2</sup>(14.696) = 0.9995  
 $G$  (sat gas, sat air) = 0.6977(0.9995)/0.9964 = 0.6999  
 $\{H_v^{id}/Z\}$ (sat gas, dry air) = 1159.1/(0.9964) = 1163.3 Btu-ft<sup>-3</sup>

## APPENDIXES

### (Nonmandatory Information)

#### X1. EFFECT OF WATER UPON THE HEATING VALUE

X1.1 Custody transfer of natural gas uses a simple pricing equation that states that the cost of gas is the rate of energy released upon combustion multiplied by the price of gas per energy unit multiplied by the time or accounting period. The rate of energy released upon combustion is the product of the heating value of the gas and the flow rate of the gas. The flow rate of the gas requires knowledge of the compressibility factor and the relative density of the gas. All three custody transfer properties (heating value, compressibility factor, and relative density) can be calculated from the composition given pure component property tables. The equations for calculating the properties of dry natural gas are well known, but this appendix also presents an account of the effects of water contained in the gas and in the air used to burn the gas.

X1.2 The heating value of a natural gas is the absolute value of its enthalpy of combustion in an ideal combustion reaction. The heating value is, therefore, an ideal gas property that can be calculated unambiguously from tables of pure component values and it has no pressure dependence.

X1.3 An ideal combustion reaction with fuel and air in the ideal gas state and the possibility of water in the fuel and air is:

$$\begin{aligned}
 & C_{\alpha}H_{\beta}S_{\gamma}(id) + (\alpha + \beta/4 + \gamma)(1 + \varepsilon)O_2(id) \quad (X1.1) \\
 & + 0.04383(\alpha + \beta/4 + \gamma)(1 + \varepsilon)Ar(id) \\
 & + [0.00162(\alpha + \beta/4 + \gamma)(1 + \varepsilon) + x_c/(1 - x_N - x_c)]CO_2(id) \\
 & + [3.72873(\alpha + \beta/4 + \gamma)(1 + \varepsilon) + x_N/(1 - x_N - x_c)]N_2(id) + (n_w^g \\
 & + n_w^a)H_2O(id) \\
 & = [\alpha + 0.00162(\alpha + \beta/4 + \gamma)(1 + \varepsilon) + x_c/(1 - x_N - x_c)]CO_2(id) \\
 & + n_w^v H_2O(id) + n_w^l H_2O(l) + \gamma SO_2(id)
 \end{aligned}$$

$$\begin{aligned}
 & + [3.72873(\alpha + \beta/4 + \gamma)(1 + \varepsilon) \\
 & + x_N/(1 - x_N - x_c)]N_2(id) \\
 & + 0.04383(\alpha + \beta/4 + \gamma)(1 + \varepsilon)Ar(id) + (\alpha + \beta/4 + \gamma)\varepsilon O_2(id)
 \end{aligned}$$

where:  $\alpha$ ,  $\beta$ , and  $\gamma$  are stoichiometric coefficients,  $\varepsilon$  is the fraction excess air, the composition of air is assumed to be that of **Table X1.1**,  $n_w^g$  and the moles of water contained in the gas,  $n_w^a$  are the moles of water contained in the air,  $n_w^v$  are the moles of water contained in the product gas mixture,  $n_w^l$  are the moles of gas that actually condense,  $X_c$  is the mole fraction of  $CO_2$  in the gas, and  $x_N$  is the mole fraction of  $N_2$  in the gas. If air has been injected into the gas, it is assumed that the effect is accounted for in the excess fraction  $\varepsilon$ . Fuel gas mixtures would have non-integer values of  $\alpha$ ,  $\beta$  and  $\gamma$ .

X1.4 It is customary to define hypothetical reference states for the water formed by the reaction denoted by **Eq 1** (as opposed to “spectator” water that enters the reaction carried by the gas or air). If we assume that the water formed in the reaction remains in the ideal gas state, the heating value is termed “net.” If we assume that the water formed in the reaction condenses totally to the liquid state, the heating value is termed “gross.” The gross heating value is greater than the net heating value by the ideal enthalpy of vaporization for water:

$$\text{heating value (gross)} - \text{heating value (net)} = H_w(id) - H_w(l) \quad (X1.2)$$

where:

$H$  = enthalpy,  
 $l$  = liquid state, and  
 $w$  = water.

**TABLE X1.1 Example Calculation of Precision**

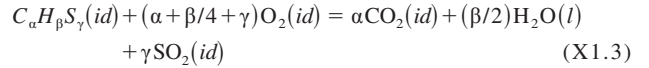
Compound	Composition, $x_j$	$H_v^{id} - H_{vi}^{id}$ Btu•ft <sup>-3</sup>	Repeatability		Reproducibility	
			$\delta x_j$	$[(H_v^{id} - H_{vi}^{id})\delta x_j]^2$ (Btu•ft <sup>-3</sup> ) <sup>2</sup>	$\delta x'_j$	$[(H_v^{id} - H_{vi}^{id})\delta x'_j]^2$ (Btu•ft <sup>-3</sup> ) <sup>2</sup>
Methane	0.8302	169.7	0.0010	0.029	0.0020	0.115
Ethane	0.0745	-590.0	0.0002	0.014	0.0004	0.056
Propane	0.0439	-1336.4	0.0002	0.071	0.0004	0.286
Isobutane	0.0083	-2072.2	0.0001	0.043	0.0002	0.171
Butane	0.0108	-2082.6	0.0002	0.173	0.0004	0.694
Isopentane	0.0031	-2821.2	0.0001	0.080	0.0002	0.318
Pentane	0.0025	-2829.2	0.0001	0.080	0.0002	0.320
Hexane	0.0030	-3576.2	0.0001	0.128	0.0002	0.512
Helium	0.0003	1179.7	0.0001	0.014	0.0002	0.056
Nitrogen	0.0032	1179.7	0.0001	0.014	0.0002	0.056
Carbon dioxide	<u>0.0202</u>	1179.7	0.0002	<u>0.056</u>	0.0004	<u>0.223</u>
Total	1.0000			0.702		2.807

The quantity  $H_w(id) - H_w(l)$  is the ideal enthalpy of vaporization for water.

X1.5 It is possible to calculate a real gas heating value rather than using a hypothetical state, but the calculations are tedious, the numerical values are negligibly different, and the mathematical simplicity of the defining equation is lost. It is customary in the gas industry to use gross heating value for most calculations, so for the remainder of this appendix, the term “heating value” refers to the gross value.

X1.6 Eq 7 in Section 7 provides the recipe to convert the heating value from one base pressure to another. Note that when using Eq 7,  $H_v^{id}$  should be calculated using the values from Table 1 before converting the pressure; the individual values in Table 1 should not be converted. Conversion to another temperature is more complicated. Heating value data

exist at 25°C based upon the reaction:



X1.7 The experiments use pure oxygen and are corrected to stoichiometric proportions. It is necessary to correct the sensible heat effects to arrive at a different temperature:

$$Hn^{id}(T) = Hn^{id}(25) + \int_{25}^T \left[ \sum_r C_p^{id} - \sum_r C_p^{id} \right] dT \quad (X1.4)$$

where:

$$\sum_r C_p^{id} = \alpha C_{p,CO_2}^{id} + (\beta/2)C_{p,H_2O}^{id} + \gamma C_{p,SO_2}^{id} \quad (X1.5)$$

$$\sum_r C_p^{id} = C_{p,C_\alpha H_\beta S_\gamma}^{id} + (\alpha + \beta/4 + \gamma)C_{p,O_2}^{id} \quad (X1.6)$$

and:  $C_p^{id}$  is the ideal specific heat at constant pressure,  $r$  denotes reactants and  $r'$  denotes products.

## X2. ACCOUNTING FOR WATER

X2.1 If the gas contains water (or must be assumed to be saturated) but the compositional analysis is on a dry basis, it is necessary to adjust the mole fractions to account for the fact that water has displaced some gas, thus lowering the heating value. The mole fraction of water in the gas results from the definition of relative humidity:

$$x_w = h^s P_w^\sigma / P = n_w / (1 + n_w) \quad (X2.1)$$

(Based upon one mole of the fuel  $C_\alpha H_\beta S_\gamma$ ) where  $h^s$  is the relative humidity of the gas,  $P_w^\sigma$  is the vapor pressure of water, and  $n_w$  denotes moles of water. For saturated gas  $h^s$  is unity. Rearranging Eq X2.1 gives the moles of water:

$$n_w = x_w / (1 - x_w) \quad (X2.2)$$

The corrected mole fractions then become:

$$x_i(\text{cor}) = x_i \left[ \frac{1}{1 + n_w} \right] = x_i \left[ \frac{1}{1 + x_w / (1 - x_w)} \right] = (1 - x_w)x_i \quad (X2.3)$$

and the heating value becomes:

$$H_v^{id} = (1 - x_w) \sum_{i=1}^N x_i^{dry} H_v_i^{id} \quad (X2.4)$$

where water is not included in the  $N$  components of the summation. If the compositional analysis determines  $x_w$  and water is included in the  $N$  components of the summation:

$$H_v^{id} = \sum_{i=1}^N x_i^{wet} H_v_i^{id} - x_w H_v_w^{id} \quad (X2.5)$$

X2.2 It is necessary to remove the effect of water because, although water has a heating value, it is only a condensation effect. Water carried by wet gas (spectator water) does not actually condense, and only water formed in the reaction contributes to heating value.

X2.3 Accounting for water in the above manner is sufficient for defined custody transfer conditions, but when trying to

model actual situations, the question becomes much more complicated. It is obvious that all of the reaction water actually cannot condense because in a situation in which both gas and air are dry some of the reaction water saturates the product gases and the remainder condenses. It is possible to account for these effects in a general manner. To do so, it is necessary to calculate  $n_w^g$ ,  $n_w^a$ ,  $n_w^v$ , and  $n_w^l$ .

$$n_w^g = (h^s P_w^\sigma / P) / [(1 - x_N - x_C) (1 - h^s P_w^\sigma / P)] \quad (X2.6)$$

$$n_w^g [1 + (x_N + x_C) / (1 - x_N - x_C) + n_w^g] = h^s P_w^\sigma / P$$

$$n_w^a [4.77418(\alpha + \beta/4 + \gamma)(1 + \epsilon) + n_w^a] = h^a P_w^\sigma / P \quad (X2.7)$$

$$n_w^a = 4.77418(\alpha + \beta/4 + \gamma)(1 + \epsilon)(h^a P_w^\sigma / P) / (1 - h^a P_w^\sigma / P)$$

$$n_w^v \{ \alpha + \gamma + (x_N + x_C) / (1 - x_N - x_C) + (\alpha + \beta/4 + \gamma) [0.001 \quad 62(1 + \epsilon) + 3.728 \quad 73(1 + \epsilon) + 0.043 \quad 83(1 + \epsilon) + \epsilon] + n_w^v \} = P_w^\sigma / P \quad (X2.8)$$

$$n_w^v = \{ \alpha + \gamma + (x_N + x_C) / (1 - x_N - x_C) + (\alpha + \beta/4 + \gamma) [0.001 \quad 62(1 + \epsilon) + 3.728 \quad 73(1 + \epsilon) + 0.043 \quad 83(1 + \epsilon) + \epsilon] \} (P_w^\sigma / P) / (1 - P_w^\sigma / P)$$

$$n_w^l = \beta/2 + n_w^g + n_w^a - n_w^v \quad (X2.9)$$

where:  $h_a$  is the relative humidity of the air. Eq X2.6 and Eq X2.7 are reformulations of Eq X2.1 to reflect inlet conditions. Eq X2.8 reflects Eq X2.1 for the saturated product gas (it must be saturated before any water can condense). Eq X2.9 is a water balance:  $\beta/2$  are the moles of water formed by the reaction,  $n_w^g + n_w^a$  are the moles of water that enter with the gas and air,  $n_w^v$  are the moles of water that saturate the product gas, and  $n_w^l$  are the moles of water that condense. Therefore, the complete correction for the effect of water on heating value is:

$$H_v^{id} = H_v^{id}(\text{Eq X2.4 or Eq X2.5}) + (h^s P_w^\sigma / P) / (1 - x_n - x_c) (1 - h^s P_w^\sigma / P) \quad (X2.10)$$



$$+ 4.77418(\alpha + \beta/4 + \gamma)(1 + \varepsilon)(h^a P_w^\sigma / P) / (1 - h^a P_w^\sigma / P) - [\alpha + \gamma + (x_n - x_c) \\ (1 - x_n - x_c) + (\alpha + \beta/4 + \gamma) (3.77418 + 4.77418 \varepsilon)] \times (P_w^\sigma / P) / (1 - P_w^\sigma) H_w^{id}$$

X2.4 Depending upon the relative humidities of the gas and air, the observed heating value can be greater or smaller than

that calculated using Eq X2.4 or Eq X2.5. A humidity of air exists for each gas above which  $Hv^{id}$  is greater than that calculated by Eq X2.4 or Eq X2.5. That critical value depends upon the gas composition, the humidity of the gas, and the amount of excess air. For pure, dry methane with no excess air,  $h_a = 0.79345$ .

### X3. REAL GAS PROPERTIES

X3.1 In principal, we have enough information to convert the heating value to a real gas property (it is not necessary to do so for relative density because the molar mass ratio,  $G^{id}$ , is the desired property). This is simply a matter of evaluating the integral:

$$Hn - Hn^{id} = \int_o^P \left\{ \left[ \left( \frac{\partial H}{\partial P} \right)_{T,r} \right] - \left[ \left( \frac{\partial H}{\partial P} \right)_{T,r} \right] \right\} dP \quad (X3.1)$$

where:

$$\left( \frac{\partial H}{\partial V} \right)_T = V - T \left( \frac{\partial V}{\partial T} \right)_P = B - T \frac{dB}{dT} = 2RT^2 b \frac{dB}{dT} \quad (X3.2)$$

where  $V$  is the molar volume. The temperature dependence of  $b$  must be defined, but in the custody transfer region it is easy to do so. The products and reactants again correspond to Eq X1.3.

X3.2 While it is obviously possible to make the required calculations to convert the heating value into a real gas property, it serves no custody transfer purpose to do so. As we have seen, the cost equation is unchanged; the calculations while obvious are tedious.  $Hv$  is slightly different from  $Hv^{id}$  because the base pressure is low; the likelihood of having all the information required to use Eq X3.1 is remote. The heating value is defined in a hypothetical state. It is not possible, at base conditions, to have all the water formed in the reaction be either all gas or all liquid; some of the water formed is in each state. Thus, if the definition is of a hypothetical state, using a hypothetical real gas rather than an ideal gas state adds nothing but complexity.

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