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International Standard 6976

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Natural gas — Calculation of calorific value, density and relative density

Gaz naturel — Calcul du pouvoir calorifique, de la masse volumique et de la densité

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Foreword

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Draft International Standards adopted by the technical committees are circulated to the member bodies for approval before their acceptance as International Standards by the ISO Council.

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Belgium	Italy	South Africa, Rep. of
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Natural gas — Calculation of calorific value, density and relative density

1 Scope and field of application

This International Standard specifies methods for the calculation of the calorific value [both superior (gross) and inferior (net)], density and relative density of natural gas when values for the physical properties of the pure components and the composition of the gas by mole fraction are known.

It also describes the determination of the precision of the calculated calorific value from the precision of the method of analysis.

Reference is made to all sources of basic data referred to for the physical properties. The conversion of basic data to the values required at the specified conditions is also given.

NOTES

1 The standard values will be revised as more accurate values for the physical properties become available from accepted sources, for example from API (American Petroleum Institute).

2 All symbols used in this International Standard are explained in annex A.

3 If the composition of the gas is given as a volume fraction, this should be converted to a mole fraction; see annex D.

4 The calorific value per unit volume of gas depends not only on the temperature and pressure but also on the degree of saturation with water vapour. Alternative methods of measurement of calorific value, for example calorimetry, are based on gas being saturated with water vapour at the specific conditions of the gas volume.

2 Definitions

For the purpose of this International Standard, the following definitions apply.

2.1 superior (gross) calorific value of a gas (relative to the volume of the dry gas): The amount of heat given out by the complete combustion of the gas with air, at a constant pressure of 1,013 25 bar and at a constant temperature t_H, of a specified volume (V) under specified conditions (t_V, p_V), all the water that is formed during the combustion being condensed at the temperature t_H.

The superior calorific value is designated:

$$H_s\ [t_H,\ V(t_V,\ p_V)]$$

NOTE — For the calorific value per mole, the indication H_s, t_H is sufficient.

2.2 inferior (net) calorific value of a gas (relative to the volume of the dry gas): The amount of heat given out by the complete combustion of the gas with air, at a constant pressure of 1,013 25 bar and at a constant temperature t_H, of a specific volume (V) under specified conditions (t_V, p_V), all the water that is formed during the combustion remaining in the gaseous phase at the temperature t_H.

The inferior (net) calorific value is designated:

$$H_i\ [t_H,\ V(t_V,\ p_V)]$$

NOTE — For the calorific value per mole the indication H_i, t_H is sufficient.

2.3 density: The mass of a gas divided by its volume under specified conditions.

2.4 relative density: The ratio of the density of a gas to the density of air under the same stated conditions of temperature and pressure.

2.5 compressibility factor: The ratio of the real volume of a given mass of gas at a specified temperature and pressure to its volume under the same conditions as calculated from the ideal gas law.

3 Principle

Methods are provided for the calculation of calorific value relative to the volume of ideal gas, and the ideal relative density and the ideal density from the specified composition and ideal values for the properties of the components. Values for the real gas are calculated from the values for the ideal gas using a calculated compressibility factor for the gas mixture.

4 Calculations (see annex A)

4.1 Calculation of ideal calorific value, ideal density and ideal relative density

Calculate the ideal calorific value H, the ideal density, ϱ, and the ideal relative density, d, of the gas mixture by means of the formulae

$$H_{(\text{ideal})} = \sum_{j=1}^{j=n} X_j H_{j\,(\text{ideal})} \qquad \ldots (1)$$

$$\varrho_{(\text{ideal})} = \sum_{j=1}^{j=n} X_j \varrho_{j\,(\text{ideal})} \qquad \ldots (2)$$

$$d_{(\text{ideal})} = \sum_{j=1}^{j=n} X_j d_{j\,(\text{ideal})} \qquad \ldots (3)$$

where

$H_{j\,(\text{ideal})}$ is the ideal calorific value (superior or inferior) of component j; values are given in tables 3 to 7 for various components, for specified conditions of temperature and pressure;

$\varrho_{j\,(\text{ideal})}$ is the ideal density of component j; values are given in table 2, for various components, for specified conditions of temperature and pressure;

$d_{j\,(\text{ideal})}$ is the ideal relative density of component j as given in table 2;

$X_{j\,(\text{ideal})}$ is the mole fraction of component j.

WARNING — The ideal values given in tables 2 to 7 have no direct physical significance for the gaseous sample and shall only be used in connection with formulae specified above.

4.2 Compressibility factor

Calculate the compressibility factor, z_{mix}, of the gas mixture, as follows [9]:

$$z_{\text{mix}} = 1 - \left(\sum_{j=1}^{j=n} X_j \sqrt{b_j} \right)^2 + 0{,}000\,5\,(2X_{\text{H}} - X_{\text{H}}^2) \qquad \ldots (4)$$

The summation factors ($\sqrt{b}$) for the respective components, except hydrogen, are given in table 8. They are calculated from the compressibility factors of the components, except for helium and carbon dioxide, using the relationship $b = 1 - z$.

Pseudo-values have been calculated for carbon dioxide and helium. [5, 6, 15]

Factors for components which are liquid under the specified conditions are obtained from the equation of state calculations for the hypothetical gas. [2, 3, 6, 9, 10a, 10b]

4.3 Real calorific value, real density and real relative density

Calculate the real calorific value, real density and real relative density of the mixture by means of the following formulae[9]:

$$H_{(\text{real})} = \frac{H_{(\text{ideal})}}{z_{\text{mix}}} \qquad \ldots (5)$$

$$\varrho_{(\text{real})} = \frac{\varrho_{(\text{ideal})}}{z_{\text{mix}}} \qquad \ldots (6)$$

$$d_{(\text{real})} = d_{(\text{ideal})} \times \frac{z_{\text{air}}}{z_{\text{mix}}} \qquad \ldots (7)$$

An example of the calculation is given in annex E.

The compressibility factor of air, z_{air}, based on Hilsenrath *et al.* [7], has the following values:

z_{air} (273,15 K) = 0,999 41

z_{air} (288,15 K) = 0,999 58

5 Precision[1)]

The precision of the method is related to the analysis. (An example is given in annex F.)

5.1 Repeatability

Calculate the repeatability ΔH as follows:

a) if all the components are analysed and if the results of the analyses are normalized, by means of the formula

$$\Delta H = [\Sigma\,(H_{(\text{ideal})} - H_{j\,(\text{ideal})})^2 \cdot \Delta X_j^2]^{1/2} \qquad \ldots (8)$$

b) if the results of analysis are made equal to 100 by calculating the methane concentration as the difference between 100 % and the sum of the concentration of the other components, by means of the formula

$$\Delta H = [\Sigma\, H_{j\,(\text{ideal})}^2 \cdot \Delta X_j^2]^{1/2} \qquad \ldots (9)$$

where, for formulae (8) and (9)

$H_{(\text{ideal})}$ is the ideal calorific value of the gas mixture;

$H_{j\,(\text{ideal})}$ is the ideal calorific value of component j;

ΔX_j is the repeatability of the method of analysis for component j.

1) Errors in calorific values of the components and in the calculated compressibility factor z_{mix}, are neglected in this International Standard.

It is expected that the calorific values determined from successive pairs of analyses, carried out by the same operator on the same sample of gas, and using the same instrument will agree within 2 ΔH in 95 % of pairs of tests when ΔX is taken as one standard deviation.

5.2 Reproducibility

The reproducibility $\Delta H'$ may be calculated by means of formulae (8) and (9) using $\Delta X'_j$, the reproducibility of the method of analysis for component j instead of ΔX_j.

The difference between real calorific values calculated from analyses performed in different laboratories is expected to exceed $\Delta H'$ in only 5 % of a large number of pairs of analyses.

Table 1 — Relative molecular masses and calorific values (per mole of pure components)

NOTE — The relative molecular masses are based on relative atomic masses for carbon (^{12}C) of 12,011 ± 0,001 and for hydrogen (^{1}H) of 1,0079 ± 0,000 1.

Components	Formula	Relative molecular mass [14]	H_s,[25] kJ/mol	H_i,[25] kJ/mol	API data sheet [2] dated
Methane	CH_4	16,042 6	890,36	802,32	1955-04-30
Ethane	C_2H_6	30,069 4	1 559,88	1 427,83	1955-04-30
Propane	C_3H_8	44,096 2	2 220,03	2 044,01	1955-04-30
Butane	C_4H_{10}	58,123 0	2 877,09	2 657,05	1955-04-30
2-Methylpropane	C_4H_{10}	58,123 0	2 868,72	2 648,68	1955-04-30
Pentane	C_5H_{12}	72,149 8	3 536,15	3 272,10	1955-04-30
2-Methylbutane	C_5H_{12}	72,149 8	3 528,12	3 264,06	1955-04-30
2,2-Dimethylpropane	C_5H_{12}	72,149 8	3 516,61	3 252,56	1955-04-30
Hexane	C_6H_{14}	86,176 6	4 194,92	3 886,81	1975-04-30
2-Methylpentane	C_6H_{14}	86,176 6	4 187,18	3 879,07	1975-04-30
3-Methylpentane	C_6H_{14}	86,176 6	4 189,82	3 881,71	1975-04-30
2,2-Dimethylbutane	C_6H_{14}	86,176 6	4 177,89	3 869,78	1975-04-30
2,3-Dimethylbutane	C_6H_{14}	86,176 6	4 185,97	3 877,86	1975-04-30
Heptane	C_7H_{16}	100,203 4	4 853,57	4 501,44	1975-04-30
2-Methylhexane	C_7H_{16}	100,203 4	4 846,49	4 494,37	1975-04-30
3-Methylhexane	C_7H_{16}	100,203 4	4 849,88	4 497,76	1975-04-30
Octane	C_8H_{18}	114,230 2	5 511,71	5 115,57	1975-04-30
2,2,4-Trimethylpentane	C_8H_{18}	114,230 2	5 496,52	5 100,38	1975-04-30
Cyclohexane	C_6H_{12}	84,160 8	3 952,92	3 688,87	1966-10-31
Methylcyclohexane	C_7H_{14}	98,187 6	4 600,64	4 292,57	1966-10-31
Benzene	C_6H_6	78,113 4	3 301,51	3 169,46	1962-04-30
Toluene	C_7H_8	92,140 2	3 947,94	3 771,88	1962-04-30
Hydrogen	H_2	2,015 8	285,84	241,83	API [1] 1945-05-31
Carbon monoxide	CO	28,010 4	282,99	282,99	API [1] 1945-05-31
Hydrogen sulphide *	H_2S	34,076	562,54	518,52	JANAF [12]
Helium	He	4,002 6			
Argon	Ar	39,948			
Nitrogen	N_2	28,013 4			
Oxygen	O_2	31,998 8			
Carbon dioxide	CO_2	44,009 8			
Water	H_2O	18,015 2 [11]			
Air		28,964 1 **			

* With sulphur dioxide as combustion product.

** Standard composition of air [7] (values expressed as mole fractions):

0,780 9 N_2
0,209 5 O_2
0,009 3 Ar
0,000 3 CO_2

Table 2 — Ideal relative densities and ideal densities

Component	Ideal relative density *, d	Ideal density **, $\varrho, V(0;1,013\ 25)$ kg·m^{-3}	Ideal density †, $\varrho, V(15;1,013\ 25)$ kg·m^{-3}
Methane	0,553 9	0,715 7	0,678 5
Ethane	1,038 2	1,341 6	1,271 7
Propane	1,522 4	1,967 4	1,865 0
Butane	2,006 7	2,593 2	2,458 2
2-Methylpropane	2,006 7	2,593 2	2,458 2
Pentane	2,491 0	3,219 0	3,051 4
2-Methylbutane	2,491 0	3,219 0	3,051 4
2,2-Dimethylpropane	2,491 0	3,219 0	3,051 4
Hexane	2,975 3	3,844 8	3,647 7
2-Methylpentane	2,975 3	3,844 8	3,644 7
3-Methylpentane	2,975 3	3,844 8	3,644 7
2,2-Dimethylbutane	2,975 3	3,844 8	3,644 7
2,3-Dimethylbutane	2,975 3	3,844 8	3,644 7
Heptane	3,459 6	4,470 6	4,237 9
2-Methylhexane	3,459 6	4,470 6	4,237 9
3-Methylhexane	3,459 6	4,470 6	4,237 9
Octane	3,943 9	5,096 5	4,831 2
2,2,4-Trimethylpentane	3,943 9	5,096 5	4,831 2
Cyclohexane	2,905 7	3,754 9	3,559 3
Methylcyclohexane	3,390 0	4,379 5	4,152 7
Benzene	2,696 9	3,485 1	3,303 7
Toluene	3,181 2	4,110 9	3,896 3
Hydrogen	0,069 6	0,089 9	0,085 2
Carbon monoxide	0,967 1	1,249 7	1,184 6
Hydrogen sulphide	1,176 5	1,520 3	1,441 2
Helium	0,138 2	0,178 6	0,169 3
Argon	1,379 2	1,782 3	1,689 5
Nitrogen	0,967 2	1,249 8	1,184 8
Oxygen	1,104 8	1,427 6	1,353 3
Carbon dioxide	1,519 5	1,963 5	1,861 3
Water (gaseous)	0,622 0	0,803 8	0,761 9
Air	1,000	1,292 2	1,225 0

* Molar mass/molar mass of air (28,964 1 g/mol).

** Molar mass/molar volume of ideal gas (volume in the following conditions: 0° C and 1,013 25 bar).

† Molar mass/molar volume of ideal gas (volume in the following conditions: 15 °C and 1,013 25 bar).

Table 3 — Ideal calorific values (superior and inferior) at 25 °C (gas volume at 0 °C and 1,013 25 bar)

Component	H_s[25, V(0;1,013 25)] kJ·m^{-3}	H_i[25, V(0;1,013 25)] kJ·m^{-3}
Methane	39 724	35 796
Ethane	69 595	63 704
Propane	99 048	91 195
Butane	128 363	118 546
2-Methylpropane	127 990	118 173
Pentane	157 768	145 987
2-Methylbutane	157 410	145 629
2,2-Dimethylpropane	156 896	145 115
Hexane	187 160	173 413
2-Methylpentane	186 814	173 068
3-Methylpentane	186 932	173 185
2,2-Dimethylbutane	186 400	172 653
2,3-Dimethylbutane	186 760	173 014
Heptane	216 546	200 835
2-Methylhexane	216 230	200 520
3-Methylhexane	216 381	200 671
Octane	245 909	228 235
2,2,4-Trimethylpentane	245 231	227 557
Cyclohexane	176 362	164 582
Methylcyclohexane	205 261	191 517
Benzene	147 299	141 408
Toluene	176 140	168 285
Hydrogen	12 753	10 789
Carbon monoxide	12 626	12 626
Hydrogen sulphide	25 098	23 134

Table 5 — Ideal calorific values (superior and inferior) at 15 °C (gas volume at 0 °C and 1,013 25 bar)

Component	H_s[15, V(0;1,013 25)] kJ·m^{-3}	H_i[15, V(0;1,013 25)] kJ·m^{-3}
Methane	39 766	35 802
Ethane	69 661	63 713
Propane	99 135	91 207
Butane	128 469	118 559
2-Methylpropane	128 096	118 186
Pentane	157 895	146 002
2-Methylebutane	157 537	145 644
2,2-Dimethylpropane	157 023	145 131
Hexane	187 306	173 429
2-Methylpentane	186 962	173 085
3-Methylpentane	187 080	173 203
2,2-Dimethylbutane	186 548	172 671
2,3-Dimethylbutane	186 908	173 031
Heptane	216 713	200 853
2-Methylhexane	216 397	200 538
3-Methylhexane	216 549	200 689
Octane	246 098	228 256
2,2,4-Trimethylpentane	245 420	227 578
Cyclohexane	176 499	164 606
Methylcyclohexane	205 415	191 539
Benzene	147 365	141 418
Toluene	176 227	168 298
Hydrogen	12 767	10 785
Carbon monoxide	12 623	12 623
Hydrogen sulphide	25 114	23 132

Table 4 — Ideal calorific values (superior and inferior) at 0 °C (gas volume at 0 °C and 1,013 25 bar)

Component	H_s[0, V(0;1,013 25)] kJ·m^{-3}	H_i[0, V(0;1,013 25)] kJ·m^{-3}
Methane	39 829	35 807
Ethane	69 759	63 727
Propane	99 264	91 223
Butane	128 629	118 577
2-Methylpropane	128 257	118 206
Pentane	158 087	146 025
2-Methylbutane	157 730	145 668
2,2-Dymethylpropane	157 215	145 153
Hexane	187 528	173 454
2-Methylpentane	187 185	173 110
3-Methylpentane	187 305	173 230
2,2-Dimethylbutane	186 772	172 698
2,3-Dimethylbutane	187 135	173 060
Heptane	216 966	200 881
2-Methylhexane	216 652	200 567
3-Methylhexane	216 805	200 721
Octane	246 381	228 286
2,2,4-Trimethylpentane	245 705	227 610
Cyclohexane	176 706	164 644
Methylcyclohexane	205 649	191 577
Benzene	147 464	141 432
Toluene	176 358	168 316
Hydrogen	12 789	10 779
Carbon monoxide	12 618	12 618
Hydrogen sulphide	25 141	23 130

Table 6 — Ideal calorific values (superior and inferior) at 15 °C (gas volume at 15 °C and 1,013 25 bar)

Component	H_s[15, V(15;1,013 25)] kJ·m^{-3}	H_i[15, V(15;1,013 25)] kJ·m^{-3}
Methane	37 696	33 938
Ethane	66 035	60 397
Propane	93 975	86 459
Butane	121 782	112 387
2-Methylpropane	121 428	112 034
Pentane	149 676	138 402
2-Methylbutane	149 336	138 062
2,2-Dimethylpropane	148 850	137 576
Hexane	177 556	164 401
2-Methylpentane	177 230	164 075
3-Methylpentane	177 342	164 187
2,2-Dimethylbutane	176 837	163 683
2,3-Dimethylbutane	177 179	164 024
Heptane	205 432	190 398
2-Methylhexane	205 133	190 099
3-Methylhexane	205 276	190 242
Octane	233 287	216 374
2,2,4-Trimethylpentane	232 645	215 732
Cyclohexane	167 311	156 037
Methylcyclohexane	194 722	181 569
Benzene	139 694	134 057
Toluene	167 054	159 537
Hydrogen	12 102	10 223
Carbon monoxide	11 966	11 966
Hydrogen sulphide	23 807	21 967

Table 7 — Ideal calorific values (superior and inferior) at 15,56 °C (gas volume at 15,56 °C and 1,013 25 bar)

Component	H_s[15,56; V(15,56;1,013 25)] kJ·m^{-3}	H_i[15,56; V(15,56;1,013 25)] kJ·m^{-3}
Methane	37 620	33 871
Ethane	65 902	60 278
Propane	93 788	86 291
Butane	121 539	112 168
2-Methylpropane	121 186	111 815
Pentane	149 378	138 132
2-Methylbutane	149 040	137 794
2,2-Dimethylpropane	148 553	137 307
Hexane	177 203	164 081
2-Methylpentane	176 877	163 754
3-Methylpentane	176 990	163 868
2,2-Dimethylbutane	176 486	163 364
2,3-Dimethylbutane	176 827	163 705
Heptane	205 024	190 027
2-Methylhexane	204 725	189 729
3-Methylhexane	204 870	189 874
Octane	232 823	215 952
2,2,4-Trimethylpentane	232 182	215 311
Cyclohexane	166 978	155 732
Methylcyclohexane	194 336	181 216
Benzene	139 420	133 796
Toluene	166 724	159 226
Hydrogen	12 079	10 205
Carbon monoxide	11 942	11 942
Hydrogen sulphide	23 760	21 885

Table 8 — Compressibility factors and summation factors for pure components at 273,15 K (0 °C), 288,15 K (15 °C) and 1,013 25 bar

NOTE — For the calculation of the compressibility factor, the critical values and values of constants (see annex B) were taken from [2]; the acentric factor was taken from [3].

Component	Compressibility factor z at 1,013 25 bar		Source (See bibliography)	Summation factor $\sqrt{b}$	
	273,15 K	288,15 K		273,15 K	288,15 K
Methane	0,997 6	0,998 0	[2] (1968-04-30)	0,049 0	0,044 7
Ethane	0,989 7	0,991 4	[2] (1971-04-30)	0,101 5	0,092 7
Propane	0,976 6	0,980 6	[2] (1971-10-31)	0,153 0	0,139 3
Butane	0,955 4	0,963 4	[2] (1972-10-30)	0,211 2	0,191 3
2-Methylpropane	0,958 3	0,965 9	[2] (1972-06-30)	0,204 2	0,184 7
Pentane	0,931 9	0,944 0		0,261 0	0,236 6
2-Methylbutane	0,939 4	0,949 9		0,246 2	0,223 8
2,2-Dimethylpropane	0,949 6	0,957 9		0,224 5	0,205 2
Hexane	0,890 0	0,911 5		0,331 7	0,297 5
2-Methylpentane	0,901 0	0,919 8		0,314 6	0,283 2
3-Methylpentane	0,900 2	0,919 3		0,315 9	0,284 1
2,2-Dimethylbutane	0,915 3	0,930 7		0,291 0	0,263 2
2,3-Dimethylbutane	0,907 2	0,924 5		0,304 6	0,274 8
Heptane	0,828 5	0,865 3	Calculated according to [10a] and [10b]	0,414 1	0,367 0
2-Methylhexane	0,845 9	0,878 1		0,392 6	0,349 1
3-Methylhexane	0,845 7	0,878 1		0,392 8	0,349 1
Octane	0,737 2	0,798 6		0,512 6	0,448 8
2,2,4-Trimethylpentane	0,823 9	0,861 1		0,419 6	0,372 7
Cyclohexane	0,897 7	0,918 3		0,319 8	0,285 8
Methylcyclohexane	0,848 1	0,881 1		0,389 7	0,344 8
Benzene	0,909 0	0,927 7		0,301 7	0,268 9
Toluene	0,848 7	0,882 4		0,390 1	0,342 9
Hydrogen	1,000 6	1,000 6	[7]	—	—
Carbon monoxide	0,999 3	0,999 5	[7]	0,026 5	0,022 4
Hydrogen sulphide	0,988 4	0,990 4	[8]	0,107 7	0,098 0
Helium	1,000 5	1,000 5	[15]	−0,016*	−0,016*
Argon	0,999 0	0,999 2	[7]	0,031 6	0,028 3
Nitrogen	0,999 5	0,999 7	[7]	0,022 4	0,017 3
Oxygen	0,999 0	0,999 3	[7]	0,031 6	0,026 5
Carbon dioxide	0,993 2	0,994 3	[7]	0,067 0*	0,061 4*
Water (gaseous)	0,968	0,971	[11]	0,179	0,170
Air	0,999 41	0,999 58	[7]	—	—

* Pseudo-value (see 4.2).