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Natural gas — Correlation between water content and water dew point

Gaz naturel — Corrélation entre la teneur en eau et le point de rosée de l'eau

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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

ISO 18453 was prepared by Technical Committee ISO/TC 193, *Natural gas*, Subcommittee SC 1, *Analysis of natural gas*.

Introduction

ISO/TC 193, *Natural gas*, was established in May 1989, with the task of creating new standards, and updating existing standards relevant to natural gas. This includes gas analysis, direct measurement of properties, quality designation and traceability.

This document provides a reliable mathematical relationship between water content and water dew point in natural gas. The calculation method was developed by GERG; it is applicable in both ways, i.e. either to calculate the water content or to calculate the water dew point. Information relating to the thermodynamic principles is given in Annex A; information relating to the traceability, applications and uncertainties associated with this work is given in Annex B.

Some of the operational problems in the natural gas industry can be traced back to water content in natural gases. Even with low water vapour content in the gas, changing operating pressure and temperature conditions can cause water to condense and thus lead to corrosion problems, hydrates or ice formation. To avoid these problems, expensive dehydration units have been installed by natural gas companies. The design and cost of these installations depend on the exact knowledge of the water content at the dew point and the (contractually) required water content.

The instruments resulting from the improvements of moisture measurement equipment during the last decades focus on the determination of water content rather than on water dew point. Therefore, if the water content is measured, a correlation is needed for the expression of water dew point.

The GERG1) Group identified a need to build a comprehensive and accurate database of measured water content and corresponding water dew point values for a number of representative natural gases in the range of interest before validating the existing correlations between water content and water dew point.

It was subsequently shown that the uncertainty range of the existing correlations could be improved.

Therefore, as a result, a more accurate, composition-dependent correlation was successfully developed on the basis of the new database.

The aim of this International Standard is to standardize the calculation procedure developed by GERG concerning the relationship between water content and water dew point (and vice versa) in the field of natural gas typically for custody transfer.

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1) GERG is an abbreviation of *Groupe Européen de Recherche Gazière*.

Natural gas — Correlation between water content and water dew point

1 Scope

This International Standard specifies a method to provide users with a reliable mathematical relationship between water content and water dew point in natural gas when one of the two is known. The calculation method, developed by GERG; is applicable to both the calculation of the water content and the water dew point.

This International Standard gives the uncertainty for the correlation but makes no attempt to quantify the measurement uncertainties.

2 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

2.1
correlation
relationship between two or several random variables within a distribution of two or more random variables

[ISO 3534-1]

NOTE The indication of the range of temperature, pressure and composition for which the correlation was validated is given in Clause 3.

2.2
working range
range of parameters for which the correlation has been validated

2.3
extended working range
range of parameters for which the correlation has been developed, but outside the range for which the correlation has been validated

2.4
uncertainty of the correlation
absolute deviation of calculated value from the experimental database

NOTE This does not include any measurement uncertainty in the field.

2.5
acentric factor
parameter to characterize the acentricity or non-sphericity of a molecule

NOTE This definition was taken from reference [1] in the Bibliography.

2.6
normal reference conditions
reference conditions of pressure, temperature and humidity (state of saturation) equal to 101,325 kPa and 273,15 K for the real, dry gas

[ISO 14532:2001]

2.6
traceability
property of the result of a measurement or the value of a standard whereby it can be related to stated references, usually national or international standards, through an unbroken chain of comparisons all having stated uncertainties

[ISO 14532:2001]

3 Development of the correlation

In the past, GERG has identified the necessity for an accurate conversion between the water content and the water dew point for natural gases with sales gas characteristics. To achieve this goal, the GERG defined a research program. In the first phase of the project, reliable data on water content together with data on water dew point were collected for several natural gases for the dew-point temperature range of interest: 15 °C to +5 °C and for the (absolute) pressure range of interest: 0,5 MPa to 10 MPa. In addition to the measurements on the seven representative natural gases, measurements were also carried out on the key binary system methane/water. The procedure used for gathering the measured data was the saturation method.

Taking the determined values for the repeatability and reproducibility of the Karl Fischer instrument as consistency criteria for all measured water contents, only a few inconsistent values were detected, which were mainly situated in the range of low water content (high pressure, low temperature range). Values which failed the consistency check were either rejected or, in a few cases, weighted much lower in the data pool. In most cases, these values were replaced by repeated measurements carried out at the same pressure and temperature conditions.

Detailed information on the experimental procedure and the composition of the natural gases used during the experiments can be found in the GERG Monograph[2].

The developed relationship is validated for dew-point temperatures ranging from 15 °C to 5 °C and (absolute) pressures ranging from 0,5 MPa to 10 MPa.

The representative natural gases used for validating the correlation were sampled technically free of glycol, methanol, liquid hydrocarbon and with a maximum content of H_2S of 5 mg/m^3 (in normal conditions). No attempt was made to investigate the impact of the uncertainties resulting from the inclusion of such contaminants.

The thermodynamic background of the developed relationship makes it possible to extend the range of applicability outside the working range to temperatures of 50 °C to 40 °C and (absolute) pressures from 0,1 MPa to 30 MPa with unknown uncertainties.

It is intended that the correlation be interpreted as reciprocal between the water content and the water dew point. Note that this relationship was derived under laboratory conditions using several compositions of natural gas sampled in the field. Under practical field operational conditions, significant additional uncertainties are generated.

Besides the uncertainty in the conversion of the measurement itself, the uncertainties of the measured values should also be considered.

Unless explicitly otherwise stated, the volume is stated under normal reference conditions (2.6).

4 Range of application and uncertainty of the correlation

4.1 Working range

The working range is within the ranges defined above, and the associated uncertainties are as follows.

a) Range of pressure: 0,5 MPa $\leqslant p \leqslant$ 10 MPa

b) Range of dew-point temperature: 15 °C $\leqslant t \leqslant$ +5 °C

c) Range of composition: the correlation accepts water and the components given in Table 1 as input parameters. The calculation method is applicable to natural gases that meet the limitations listed in Table 1. Examples of the influence of composition are given in Annex C.

Table 1 — Range of composition for percentage molar composition

Compound	Percentage molar composition
Methane (CH_4)	$\geqslant$ 40,0 %
Nitrogen (N_2)	$\leqslant$ 55,0 %
Carbon dioxide (CO_2)	$\leqslant$ 30,0 %
Ethane (C_2H_6)	$\leqslant$ 20,0 %
Propane (C_3H_8)	$\leqslant$ 4,5 %
2-Methyl propane (C_4H_{10})	$\leqslant$ 1,5 %
n-Butane (C_4H_{10})	$\leqslant$ 1,5 %
2,2-Dimethyl propane (C_5H_{12})	$\leqslant$ 1,5 %
2-Methyl butane (C_5H_{12})	$\leqslant$ 1,5 %
n-Pentane (C_5H_{12})	$\leqslant$ 1,5 %
C_{6+} (sum of hexane + higher hydrocarbons) (C_6H_{14})	$\leqslant$ 1,5 %
NOTE C_{6+} is treated as *n*-hexane.	

Within the range above the uncertainty are the following:

for the water dew point calculated from the water content: 2 °C

for the water content calculated from the water dew point:

1) ${}_N$ 580 mg/m^3: 0,14 + 0,021 ${}_N$ 20 (mg/m^3);

2) ${}_N \geqslant$ 580 mg/m^3: 18,84 + 0,053 7 ${}_N$ 20 (mg/m^3).

For the application of these formulae, refer to Annex B and the examples given in Annex C.

NOTE The conversion between normal reference conditions and standard reference conditions is given in ISO 13443.

4.2 Extended working range

Extension of the application range may be extrapolated within the following ranges, but the associated uncertainties are unknown.

a) Range of pressure: extended range of (absolute) pressure is 0,1 MPa $\leqslant p$ 0,5 MPa and 10 MPa $p \leqslant$ 30 MPa;

b) Range of temperature: extended range of dew-point temperature is 50 °C ⩽ t 15 °C and +5 °C t ⩽ +40 °C;

c) Range of composition: range of components is the same as in 4.1.

5 Correlation

5.1 General

The correlational method is based on the Peng and Robinson equation of state (see Annex A for detailed information).

In order to ensure an accurate calculation of water vapour pressure above ice and liquid, it was decided to divide the new -function into two parts:

the temperature range of 223,15 K to 273,16 K, i.e. vapour pressure data above ice;

the temperature range of 273,16 K to 313,15 K, i.e. vapour pressure data over liquid water.

$$T_\mathrm{R} \qquad {}^{2}$$

where T_R is the reduced temperature as follows:

$$T_\mathrm{R} \quad \frac{T}{T_\mathrm{crit}}$$

The coefficients of the new -function are listed as follows.

a) For the range: 223,15 K ⩽ T 273,16 K

1) A_1 = 0,106 025

2) A_2 = 2,683 845

3) A_3 = 4,756 38

b) For the range: 273,16 K ⩽ T 313,15 K

1) A_1 = 0,905 436

2) A_2 = 0,213 781

3) A_3 = 0,260 05

A reliable estimate for the parameter was obtained from an appropriate set of vapour-liquid equilibria data.

The optimum parameters for binary parameters k_{ij} are found by satisfying a specified statistical criterion (minimization of an objective function through a least squares fit algorithm). For the binary systems, carbon dioxide/water, methane/water and ethane/water, it was necessary to introduce temperature-dependent interaction parameters to obtain a satisfactory description of the vapour-liquid equilibrium. The temperature dependence is given as:

$$k_{ij} \qquad {}_{ij,0} \quad {}_{ij,1}$$

This definition of $k_{ij}(T)$ has the advantage that k_{ij} equals $k_{ij,0}$ when the temperature equals 0 °C. The parameters of the binary water system are optimized for the extended working range of this correlation (50 °C up to 40 °C). Extrapolation of the data beyond the extended working range is not allowed.

Pure component data are listed in Table 2 and an overview over the complete binary interaction parameters is given in Table 3.

Table 2 — Pure component data (compound properties used in the calculation)

Component		p_c	T_c	**Source**
Water (H_2O)	0,344 37	220,64	647,14	Knapp (1982) [12]
Nitrogen (N_2)	0,035 93	33,99	126,26	Knapp (1982) [12]
Carbon dioxide (CO_2)	0,223 94	73,86	304,21	Knapp (1982) [12]
Methane (CH_4)	0,011 4	45,99	190,55	Knapp (1982) [12]
Ethane (C_2H_6)	0,099 09	48,72	305,33	Knapp (1982) [12]
Propane (C_3H_8)	0,156 11	42,46	369,85	Knapp (1982) [12]
2–Methyl propane (*i*-C_4H_{10})	0,184 65	36,4	407,85	Knapp (1982) [12]
n–Butane (*n*-C_4H_{10})	0,197 77	37,84	425,14	Knapp (1982) [12]
2,2–Dimethyl propane (*neo*-C_5H_{12})	0,195 28	31,96	433,75	Knapp (1982) [12]
2–Methyl butane (*i*-C_5H_{12})	0,226 06	33,7	460,39	Knapp (1982) [12]
n–Pentane (*n*-C_5H_{12})	0,249 83	33,64	469,69	Knapp (1982) [12]
n–Hexane (C_6H_{14})	0,296	30,2	507,85	Knapp (1982) [12]

is the acentric factor

p_c is the critical pressure, expressed in bar

T_c is the critical temperature, expressed in kelvins

Table 3 — Binary interaction parameters

Component i	Component j	$k_{ij,0}$	$k_{ij,1}$	Source
Water	Nitrogen	0,480 0	0	GERG [2]
Water	Carbon dioxide	0,184	0,236	GERG [2]
Water	Methane	0,651	1,385	GERG [2]
Water	Ethane	0,635	0,93	GERG [2]
Water	Propane	0,53	0	GERG [2]
Water	*n*-Butane	0,69	0	GERG [2]
Water	*n*-Pentane	0,5	0	GERG [2]
Water	*n*-Hexane	0,5	0	GERG [2]
Water	2-Methyl propane	0,69	0	GERG [2]
Water	2,2-Dimethyl propane	0,5	0	GERG [2]
Water	2-Methyl butane	0,5	0	GERG [2]
Nitrogen	Carbon dioxide	0,017 0	0	Knapp (1982) [9]
Nitrogen	Methane	0,031 1	0	Knapp (1982) [9]
Nitrogen	Ethane	0,051 5	0	Knapp (1982) [9]
Nitrogen	Propane	0,085 2	0	Knapp (1982) [9]
Nitrogen	*n*-Butane	0,080 0	0	Knapp (1982) [9]
Nitrogen	*n*-Pentane	0,100 0	0	Knapp (1982) [9]
Nitrogen	*n*-Hexane	0,149 6	0	Knapp (1982) [9]
Nitrogen	2-Methyl propane	0,103 3	0	Knapp (1982) [9]
Nitrogen	2,2-Dimethyl propane	0,093 0	0	Avlonitis (1994) [8]
Nitrogen	2-Methyl butane	0,092 2	0	Knapp (1982) [9]
Carbon dioxide	Methane	0,091 9	0	Knapp (1982) [9]
Carbon dioxide	Ethane	0,132 2	0	Knapp (1982) [9]
Carbon dioxide	Propane	0,124 1	0	Knapp (1982) [9]
Carbon dioxide	*n*-Butane	0,133 3	0	Knapp (1982) [9]
Carbon dioxide	*n*-Pentane	0,122 2	0	Knapp (1982) [9]
Carbon dioxide	*n*-Hexane	0,110 0	0	Knapp (1982) [9]
Carbon dioxide	2-Methyl propane	0,120 0	0	Knapp (1982) [9]
Carbon dioxide	2,2-Dimethyl propane	0,126 0	0	Kordas (1994) [10]
Carbon dioxide	2-Methyl butane	0,121 9	0	Knapp (1982) [9]
Methane	Ethane	0,002 6	0	Knapp (1982) [9]
Methane	Propane	0,014 0	0	Knapp (1982) [9]
Methane	*n*-Butane	0,013 3	0	Knapp (1982) [9]
Methane	*n*-Pentane	0,023 0	0	Knapp (1982) [9]
Methane	*n*-Hexane	0,042 2	0	Knapp (1982) [9]
Methane	2-Methyl propane	0,025 6	0	Knapp (1982) [9]
Methane	2,2-Dimethyl propane	0,018 0	0	Kordas (1995) [11]
Methane	2-Methyl butane	0,005 6	0	Knapp (1982) [9]
Ethane	Propane	0,001 1	0	Knapp (1982) [9]

Table 3 (*continued*)

Component i	**Component** j	$k_{ij,0}$	$k_{ij,1}$	**Source**
Ethane	*n*-Butane	0,009 6	0	Knapp (1982) [9]
Ethane	*n*-Pentane	0,007 8	0	Knapp (1982) [9]
Ethane	*n*-Hexane	0,010 0	0	Knapp (1982) [9]
Ethane	2-Methyl propane	0,006 7	0	Knapp (1982) [9]
Ethane	2,2-Dimethyl propane	0,023 0	0	Nishiumi (1988) [7]
Ethane	2-Methyl butane	0,016 0	0	Nishiumi (1988) [7]
Propane	*n*-Butane	0,003 3	0	Knapp (1982) [9]
Propane	*n*-Pentane	0,026 7	0	Knapp (1982) [9]
Propane	*n*-Hexane	0,000 7	0	GERG [2]
Propane	2-Methyl propane	0,007 8	0	Knapp (1982) [9]
Propane	2,2-Dimethyl propane	0	0	
Propane	2-Methyl butane	0,011 1	0	Knapp (1982) [9]
2-Methyl propane	*n*-Butane	0,000 4	0	GERG [2]
2-Methyl propane	*n*-Pentane	0	0	
2-Methyl propane	*n*-Hexane	0	0	
2-Methyl propane	2,2-Dimethyl propane	0	0	
2-Methyl propane	2-Methyl butane	0	0	
n-Butane	*n*-Pentane	0,017 4	0	Knapp (1982) [9]
n-Butane	*n*-Hexane	0,005 6	0	K-BP [2] [12]
n-Butane	2,2-Dimethyl propane	0	0	
n-Butane	2-Methyl butane	0	0	
2,2-Dimethyl propane	2-Methyl butane	0	0	
2,2-Dimethyl propane	*n*-Pentane	0	0	
2,2-Dimethyl propane	*n*-Hexane	0	0	
2-Methyl butane	*n*-Pentane	0,060	0	Knapp (1982) [9]
2-Methyl butane	*n*-Hexane	0	0	
n-Pentane	*n*-Hexane	0	0	

5.2 Input and output

5.2.1 Input

The input parameters for the water content/water dew point correlation are:

a) dry gas composition (mol %),

b) absolute pressure (bar),

c) water content (mg/m^3) *or* water dew point (°C).

5.2.2 Output

The correlation calculates either the water dew point (°C) or the water content (mg/m^3).

Annex A
(normative)

Thermodynamic principles

NOTE This annex provides more details to Clause 5 and reference [6] describes a PC program for calculating the water content or water dew point.

A.1 Phase equilibrium thermodynamics

A.1.1 General

The second principle of thermodynamics defines the state of thermodynamic equilibrium of a closed system as the state of maximum entropy. The entropy, S, of an isolated system can only increase, therefore the initial state of equilibrium of an isolated system is stable.

When a system is perturbed in the region of equilibrium it returns to equilibrium as soon as the perturbation has ceased. In some cases, the return to equilibrium can take an infinite time; this is referred to as asymptotic stability. Thus the condition of equilibrium is written as follows:

$$0 \tag{A.1}$$

This perturbation can be developed for all orders:

$$\frac{1}{2!}{}^{2} \quad \frac{1}{3!}{}^{3} \quad \frac{1}{4!}{}^{4} \quad \ldots \tag{A.2}$$

where denotes the differential forms.

When the terms for all orders greater than 1 are negative:

$${}^{2} \quad {}^{3} \quad {}^{4} \quad 0 \quad \ldots \tag{A.3}$$

the equilibrium is said to be stable.

When the second order term is positive:

$${}^{2} \quad 0 \tag{A.4}$$

the equilibrium is said to be unstable.

When some of the higher order terms are positive:

$${}^{2} \quad {}^{3} \quad {}^{4} \quad 0 \tag{A.5}$$

the equilibrium is said to be metastable.

The limit of metastability is defined by the following:

$${}^{2}S \quad 0 \tag{A.6}$$

The study of the thermodynamic state of equilibrium of a system is conducted on the basis of thermodynamic potentials; in terms of Gibbs' free energy, G, at fixed T and p, the state of equilibrium is defined by a minimum:

$$\mathrm{d}G = 0, \quad \mathrm{d}^2G > 0 \tag{A.7}$$

In the same way, at fixed T and V the state of equilibrium will be defined by the minimum of Helmholtz free energy A. For a system including "nc" constituents distributed over "$n\varphi$" phases, the free energy to be minimized is:

$$G = \sum_{j=1}^{n\varphi} \sum_{i=1}^{nc} n_{ij}\,\mu_{ij} \tag{A.8}$$

with the following constraints

$$\sum_{j=1}^{n\varphi} n_{ij} = n_i \tag{A.9}$$

where

n_i is the total number of moles of constituent i;

n_{ij} is the number of moles of constituent i in phase j;

μ_{ij} is the chemical potential of constituent i in phase j.

The direct search for a state of equilibrium is thus a minimizing of a function of ($n\varphi \cdot nc$) variables under nc constraints. The simplicity of this statement of the problem masks the practical difficulties of such a search.

Applying the first law of thermodynamics for a homogeneous closed system, more specifically pure or constant composition fluids, the following equation is obtained.

$$\mathrm{d}U = \mathrm{d}W + \mathrm{d}Q \tag{A.10}$$

In a reversible process, from the Second Law of Thermodynamics

$$\mathrm{d}W = -p\mathrm{d}V \tag{A.11}$$

and

$$\mathrm{d}Q = T\mathrm{d}S \tag{A.12}$$

Combining Equations (A.10), (A.11) and (A.12) gives

$$\mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V \tag{A.13}$$

A heterogeneous closed system contains two or more phases. In such a system, each phase may be viewed as a homogeneous open system, because any component in the system may move across the phase boundaries from one phase to another.

The internal energy, U, of a homogeneous open system is dependent on additional variables: the quantity of each component in the system. The quantity of the components may be represented by the number of moles of the components.

For an open system containing N components,

$$U = U(S,V,n_1,n_2,\ldots n_N) \tag{A.14}$$

Applying the chain rule to Equation (A.14) to obtain total differential gives

$$\mathrm{d}U \qquad S,n \qquad {}^{N}_{i} \qquad \mathrm{d}n_i \quad {}_{S,V,n_j} \tag{A.15}$$

where j represents all components other than i.

Since

$$\begin{aligned} &\qquad\qquad T \\ &V \\ &\qquad\qquad p \\ &S \end{aligned} \tag{A.16}$$

Then combining Equations (A.15) and (A.16) gives

$$\mathrm{d}U \quad T\,\mathrm{d}S \quad p\,\mathrm{d}V \quad {}^{N}_{i} \qquad {}_{S,V,n_j}\,\mathrm{d}n_i \tag{A.17}$$

The partial derivative $\;{}_{S,V,n_j}$ is called “chemical potential” and is customarily denoted by

$$_i \qquad {}_{S,V,n_j} \tag{A.18}$$

In 1923, G.N. Lewis introduced the fugacity, f, which is equivalent to the chemical potential and is expressed in units of pressure.

$$\mathrm{d}\;_i \quad RT\mathrm{d}\;\ln f_i \tag{A.19}$$

In real gases, the fugacity may be considered as a corrected partial pressure, which is shown by the fugacity coefficient

$$_i \quad \frac{f_i}{x_{i,\mathrm{v}} \quad p} \tag{A.20}$$

where $x_{i,\mathrm{v}}$, the mole fraction of a component i in the vapour phase considered.

The fugacity coefficient indicates the deviation to the ideal gas law. Therefore, for ideal gases, the fugacity coefficient becomes unity.

A.1.2 Conditions for equilibrium

The equality of chemical potentials of each constituent in the two phases is a necessary condition for equilibrium:

$$_{i,\mathrm{v}} \text{ for any } i \quad 1 \text{ to } nc$$

The same applies to the following fugacities:

$$f_{i,\mathrm{l}} \quad f_{i,\mathrm{v}} \text{ for any } i \quad 1 \text{ to } nc$$

and to the temperatures and pressures:

$$T_{i,\mathrm{l}} \quad T_{i,\mathrm{v}} \text{ for any } i \quad 1 \text{ to } nc$$

Most equilibrium calculation algorithms rely on these conditions.

When this condition is reached, the equilibrium coefficients are identified with the ratio of the fugacity coefficients:

$$K_i \quad \frac{{}_{i,\mathrm{l}}}{{}_{i,\mathrm{v}}} \text{ for any } i \quad 1 \text{ to } nc$$

In a two-component vapour-liquid equilibrium system (index v=vapour, l=liquid) the set of equations is reduced to:

$$T^{\mathrm{l}} \quad T^{\mathrm{v}}$$

$$p^{\mathrm{l}} \quad p^{\mathrm{v}} \qquad \text{(A.21)}$$

$$f_i^{\mathrm{l}} \quad f_i^{\mathrm{v}}(i \quad 1{,}2)$$

An equilibrium condition (A.7) can be derived for each component i from the equilibrium of matter (A.21) using the definition of the fugacity coefficient (A.20), where x_i is the mole fraction of component i in the liquid phase and y_i is the mole fraction in the gaseous phase.

$$^{\mathrm{l}} \quad {}_i^{\mathrm{v}} y_i (i \quad 1....N) \qquad \text{(A.22)}$$

The relationship between the fugacity coefficient of a component i in any phase and the state variables of this phase usually are linked to thermal equations of state. For an equation of state, explicit in pressure, the fugacity coefficient reads:

$$\ln \ _i \quad \frac{1}{RT}\ _V \qquad \mathrm{d}V \quad \ln Z \qquad \text{(A.23)}$$

with compressibility factor Z

$$Z \quad \frac{pV}{nRT} \qquad \text{(A.24)}$$

The compressibility factor is a measure of the deviation from the ideal gas law, for which Z equals unity.

A.2 Equations of state

A.2.1 Pure compounds

Thermal equations of state give a relationship between the pressure p, the volume V and the temperature T for a pure compound.

$$f(p,V,T) \quad 0 \qquad \text{(A.25)}$$

The most simple equation of state is the ideal gas law:

$$pV \quad nRT \tag{A.26}$$

The ideal gas model is based on the assumptions that molecules do not interact with each other and their inherent volume is negligible. So, the ideal gas law is valid for low densities only, where these assumptions (nearly) are justified. Because of the neglected attractive forces between the molecules, condensed phases cannot be described with this model. To overcome these restrictions, many equations of state have been developed, which include the ideal gas law as boundary condition. The equations may be divided into groups as follows[13] [14]:

semi-empirical (cubic) equations, Peng-Robinson, Soave-Redlich-Kwong, etc.;

modified virial equations, the virial equation being the only theoretical equation;

pVT-calculations based on the principle of corresponding states;

equations based on statistical thermodynamics.

In this annex, only a selected part of these groups will be discussed. Emphasis is put on semi-empirical (cubic) equations which form the basis for the new calculation method (BWT). For a more detailed description of the other groups, the treatises by Dohrn[13], Walas[15] and Anderko[16] may be recommended.

The first cubic equation of state was developed by J.D. Van der Waals in 1873[18] as follows:

$$\frac{RT}{V_m \quad b} \quad \frac{a}{V_m^2} \qquad p_{\text{attraction}} \tag{A.27}$$

Attractive forces between the molecules are taken into account by the correction term for pressure $\frac{a}{V_m^2}$. The quantity b is called the covolume. It is a measure for the inherent volume of the molecules and characterizes the repulsive forces. The Van der Waals (VDW) equation was the first one, which succeeded in a quantitative reproduction of the behaviour of fluids in the gas and liquid phase simultaneously (with one equation, only). But it turned out that this equation shows insufficient accuracy for many applications. Therefore, numerous cubic equations have been developed in the last century, which often retain the division into attraction and repulsion terms. Though all those modifications differ in many details, they may be reduced to a general five parameter structure[13] [16] [17].

$$p \quad \frac{RT}{V_m \quad b} \quad \frac{\ldots}{V_m \quad ,} \tag{A.28}$$

The variables , , , for some important cubic equations of state are given in Table A.1.

Table A.1 — Variables for Equation (A.28)

Equation of state	Abbreviated term				
Van der Waals (1873) [18]	VDW	a	0	0	b
Soave-Redlich-Kwong (1972) [19]	SRK	$a(T)$	b	0	b
Peng-Robinson (1976) [20]	PR	$a(T)$	$2b$	b^2	b
Patel-Teja (1982) [17] [21]	PT	$a(T)$	$b+c$	cb	b

For the two-parameter equations, both parameters (a and b) can be determined from the critical point condition. The critical isotherm of a pure fluid exhibits a saddle point in the p,V-diagram, at the critical point.

$$\frac{p}{V_m}_{T \; T_{\text{crit}}} \quad 0; \qquad \frac{{}^2p}{V_m^2}_{T \; T_{\text{crit}}} \quad 0; \tag{A.29}$$

For equations with more than two parameters, additional boundary conditions have to be defined.

Among all the improvements of the Van der Waals (VDW) equation, the Peng-Robinson (PR) Equation [20] stands out. Originally developed for gas condensate systems, it proceeded as a standard tool in many applications. Compared to VDW, the PR-equation has a modified attraction term only. The PR-equation reads:

$$p \;\; T,V_m \qquad \frac{R \;\; T}{V_m \;\; b} \quad \frac{a}{V_m^2 \;\; 2bV_m \;\; b^2} \tag{A.30}$$

From the critical point conditions [Equation (A.31)] follows:

$$a \qquad 0,457\ 24 \; \frac{R^2 \;\; T_{\text{crit}}{}^2}{p_{\text{crit}}} \tag{A.31}$$

$$b \qquad 0,077\ 80 \; \frac{R \;\; T_{\text{crit}}}{p_{\text{crit}}} \tag{A.32}$$

For temperatures different from T_{crit}, a temperature-dependent function (T_{R}) is introduced, to obtain a better reproduction of the vapour pressure curve.

$$a \;\; T \qquad a \;\; T_{\text{crit}} \qquad T_{\text{R}} \tag{A.33}$$

$$T_{\text{R}} \quad \frac{T}{T_{\text{crit}}} \tag{A.34}$$

Term (T_{R}) is a non-dimensional function of the reduced temperature T_{R}. At the critical temperature, it becomes unity. The b-parameter of the PR-equation is temperature independent.

Peng and Robinson found the functional form for the -term using vapour pressures from literature. They formed a linear relationship between $^{1/2}$ and $T_{\text{R}}{}^{1/2}$:

$$T_{\text{R}} \;\; {}^{1/2} \qquad 1 \qquad 1 \quad T_{\text{R}}{}^{1/2} \tag{A.35}$$

The coefficient is a substance specific constant, which is generalized using the acentric factor

$$0,374\ 64 \quad 1,542\ 26 \qquad 0,269\ 92 \;\; {}^2 \tag{A.36}$$

A.2.2 Mixtures

To apply equations of state for the calculations of mixture properties, the equation parameters (a, b, ...) of the pure compounds have to be substituted by mixture parameters (a_{m}, b_{m}, ...). The relationship between mixture parameters and pure compound parameters is established by mixing rules. This procedure is based on the "one-fluid"-theory[13]. It is assumed, that a (hypothetical) pure fluid exists, which behaves (under the given conditions p, T) similar to the mixture. The simplest mixing rules available, are the symmetric rules developed by Van der Waals. For a two-parameter equation of state, it reads:

$$a_M(T) \quad \overset{n \quad n}{\underset{i\ 1\ j\ 1}{}} \quad x_i x_j a_{ij} \tag{A.37}$$

$$b_M \quad \overset{n}{\underset{i\ 1}{}} \quad x_i b_i \tag{A.38}$$

$$a_{ij} \ T \quad \sqrt{a_{ii} a_{jj}} \tag{A.39}$$

$$k_{ij} \quad k_{ji} \tag{A.40}$$

$$k_{ii} \quad k_{jj} \quad 0 \tag{A.41}$$

The mole fraction x_i of the several components in the mixture is used as a weight factor for the parameters. Additionally, the cross coefficients a_{ij} of the a-term are corrected with a binary interaction parameter k_{ij}. These k_{ij}-values frequently are determined by fitting to vapour liquid equilibrium data of binary mixtures. Though interaction parameters obtain only small values in most cases, they have a strong influence on the reproducibility of phase equilibria, particular at high pressures. In the literature, many mixing rules and modifications exist[22], which provide several problem specific advantages (e.g. references [23], [24] and [28]).

A.3 Phase behaviour

From the equilibrium conditions follows, that some of the intensive state variables and compositions in the various phases cannot be chosen independently for a system, which is in equilibrium. For a heterogeneous system, the number of free eligible variables is determined by Gibbs's phase rule[25] [26]:

$$F \quad 2 \quad P \quad N \tag{A.42}$$

where

F are the number of degrees of freedom;

N are the number of compounds;

P are the number of phases.

With this phase rule (A.25), it can be derived that the most crucial quantities for the water content in the gaseous phase are pressure, temperature and the gas composition. These main quantities influence the intermolecular forces and the phase equilibrium. The influence of the gas composition depends strongly on the substances present in the gas, especially for gas mixtures with strongly different molecular properties. In this respect, an essential quantity is the molecular charge distribution[27]. This charge distribution affects the phase equilibrium particular at high densities, i.e. at high pressures, or in liquids. The hydrocarbons, occurring in natural gases, are non or weak polar substances. Water however, belongs to the strong polar substances, due to its high dipole momentum. The hydrogen bonding between water molecules in the dense liquid phase enables the formation of gas hydrates (clathrates).

Annex B
(informative)

Traceability

B.1 General

The correlation is based upon an initial determination of a known water content, using an appropriate ISO test method, from which can be derived by means of this correlation, a water dew point having due regard to the practical operational limitations expressed in B.2 to B.4.

B.2 Traceability

This particular correlation is considered only to give a traceable expression when starting with an input parameter that can be directly compared through an unbroken chain of comparisons to a national or International Standard.

Due to the presence of contaminants in natural gas and its non-ideal behaviour under elevated pressures, a direct water dew point determination cannot be compared to an International Standard without introducing significant unquantifiable uncertainties.

Therefore, using a water dew point value determined in the field as the input parameter will not give a traceable expression for the water content. In addition, an expression of uncertainty will need to be determined in order to reflect the uncertainty associated with making a direct field determination, such as variations in temperature, pressure and testing methodology that will apply at each sampling point.

The temperature at which any condensation (dew point) can commence is influenced, amongst other things, by the impurities present in the gas stream. Therefore the uncertainty associated with an input of dew point determined on a gas containing normal contaminants cannot be assessed.

B.3 Uncertainty of the correlation

Statements of uncertainty herein are described relating to the determination of water content and water dew point. It should be noted that these have been generated under laboratory conditions and represent the best practice with natural gases as previously described. Attempts to determine an accurate field value for water dew point in natural gas are hampered by the presence of any contaminants such as methanol, glycol or liquid hydrocarbons, which will affect the water vapour equilibrium along the pipeline giving rise to a range of condensation points rather than one absolute value. As such there are greater uncertainties associated with these direct determinations than with the measurement of a water content. These practical considerations have a significance in the application of the correlation.

B.4 Applicability

The main application of this correlation is in the case of gas transport and custody transfer where “technically” clean natural gas is being transported. In such cases, the correlation gives a traceable expression of the water dew point when using a traceably determined water content as the input value. The facility to express traceably determined water content as a water dew point can help companies avoid the need to change units for those gas contracts that have been historically understood in terms of water dew point.

For gas-producing companies, desiccants, liquid hydrocarbons and other contaminants are usually present in the gas pipelines and facilities. Wherever there is a presence of methanol, liquid hydrocarbons or glycol it is possible to establish an equilibrium between the glycol/water/hydrocarbon mixture that changes along the pipe. In such cases “water dew point” has no sensible physical meaning. In such instances the correlation is not deemed to be suitable for upstream areas, unless starting with a known water content in order to predict a likely range of dew points that may be encountered.

The third situation concerns gas transport from production to treatment facilities in a two-phase flow pipeline. This is particularly relevant to offshore production. As in the second situation, contaminants such as methanol or glycol are usually present as carryover changing the vapour equilibrium and again it is not meaningful to use the term dew point as a measure of the water vapour content of the gas. The liquid hydrocarbons contain dissolved and/or dispersed water and may interfere with the establishment of an equilibrium between the water/glycol mixture and the water vapour in the gas. In such situations, it is again probably more appropriate to work in terms of water vapour concentration.

However, this correlation is valuable in process simulation for predicting a water dew point from a known water content and this correlation generates more reliable simulation data within processes for many pressure vessel applications where corrosion or hydrate formation is possible.

Annex C
(informative)

Examples of calculations

C.1 Examples of water dew point calculations with different gas compositions

C.1.1 Input

$_N$ = 60 mg/m^3 (i.e. measurement)

Gas composition and pressure as specified in Table C.1.

C.1.2 Output

Dew point temperature T as specified in Table C.1 (uncertainty of 2 °C).

Table C.1 — Example of water dew point calculation with different gas compositions

Dry gas composition	p(absolute) = 2 MPa T (°C)	p(absolute) = 5 MPa T (°C)	p(absolute) = 8 MPa T (°C)
90 % methane, 8 % ethane, 2 % propane	16,3	6,7	2,0
80 % methane, 13 % ethane, 4 % propane, 3 % carbon dioxide	16,3	6,8	2,2
75 % methane, 16 % ethane, 4,5 % propane, 4,5 % carbon dioxide	16,4	6,9	2,2
70 % methane, 20 % ethane, 4,5 % propane, 5,5 % carbon dioxide	16,4	6,9	2,1

C.2 Examples of water content calculations with different gas compositions

C.2.1 Input

Dew point temperature T = 5 °C (i.e. contractual specification).

Gas composition and pressure as specified in Table C.2.

C.2.2 Output

$_N$ as specified in Table C.2 (uncertainty to be calculated as indicated in 4.1 and examples are given in C.3).

Table C.2 — Examples of water content calculations with different gas compositions

Dry gas composition	p(absolute) = 2 MPa $_N$ (mg/m^3)	p(absolute) = 5 MPa $_N$ (mg/m^3)	p(absolute) = 8 MPa $_N$ (mg/m^3)
90 % methane, 8 % ethane, 2 % propane	167,3	70	45,3
80 % methane, 13 % ethane, 4 % propane, 3 % carbon dioxide	168,5	70,9	46,1
75 % methane, 16 % ethane, 4,5 % propane, 4,5 % carbon dioxide	169	71,3	46,3
70 % methane, 20 % ethane, 4,5 % propane, 5,5 % carbon dioxide	169	71,1	45,7

C.3 Examples of the calculation for the uncertainty in the water content

C.3.1 Example 1: Calculation of uncertainty for $_N$ = 100 mg/m^3

Uncertainty: (0,14 + 0,021 100 20) mg/m^3

0,14 + 2,1 20 upper uncertainty: + 22,24 mg/m^3

lower uncertainty: 17,76 mg/m^3

$_N$ upper: 100 + 22,24 = 122,24 mg/m^3

$_N$ lower: 100 17,76 = 82,24 mg/m^3

Therefore: 82,24 mg/m^3 $\leqslant$ $_N$ $\leqslant$ 122,24 mg/m^3

C.3.2 Example 2: Calculation of uncertainty for $_N$ = 600 mg/m^3

Uncertainty: (18,84 + 0,053 7 600 20) mg/m^3

18,84 + 32,22 20 upper uncertainty: + 33,38 mg/m^3

lower uncertainty: 6,62 mg/m^3

$_N$ upper: 600 + 33,38 = 633,38 mg/m^3

$_N$ lower: 600 6,62 = 593,38 mg/m^3

Therefore: 593,38 mg/m^3 $\leqslant$ $_N$ $\leqslant$ 633,38 mg/m^3

Annex D
(informative)

Subscripts, symbols, units, conversion factors and abbreviations

D.1 Subscripts, symbols and units

D.1.1 Subscripts

c	At critical point
R	Reduced conditions
v	Vapour phase
w	Water

D.1.2 Symbols and units

b	Co-volume parameter	m^3/kmol
x	Mole fraction	
p	(absolute) pressure	kPa
R	Gas constant (8,314 510)	J/(K mol)
t	Celsius temperature	C
T	Thermodynamic (absolute) temperature	K
V	Volume	m^3
V_m	Molar volume	m^3/kmol
$_N$	Mass concentration of water content	mg/m^3 (in normal conditions)
k_{ij}	Binary interaction parameter	
	Substance-dependent acentric factor	
	Substance-dependent constant	

D.2 Conversion factors for pressure, temperature, volume and volumic mass

D.2.1 Pressure

To convert from

kPa	to	bar	Use the formula	$\text{bar} \quad \frac{\text{kPa}}{100}$	
MPa	to	bar	Use the formula	bar = MPa 10	
atm	to	bar	Use the formula	bar = atm 1,013 25	
psia	to	bar	Use the formula	$\text{bar} \quad \frac{\text{psia}}{14{,}503\,8}$	(approximate)
psig	to	bar	Use the formula	$\text{bar} \quad \frac{\text{psig}+14{,}695\,9}{14{,}503\,8}$	(approximate)

D.2.2 Temperature

To convert from

K to C Use the formula °C = K 273,15

D.2.3 Volume

To convert from

m^3(standard conditions) to m^3(normal conditions) Use the formula m^3(n.c.) = m^3(s.c.) 0,947 (approximate for natural gas)

D.2.4 Volumic mass

To convert from

ppm to mg/m^3 (normal conditions) Use the formula mg/m^3 = ppm 1,245 (approximate for water)

D.3 List of abbreviated terms

ASTM	American Society for Testing and Materials
CEN	European Committee for Standardisation
GERG	Groupe Européen de Recherches Gazières
IEC	International Electrotechnical Commission
IGU	International Gas Union
ISO	International Organization of Standardization

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