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Refrigerated hydrocarbon liquids — Static measurement — Calculation procedure

Hydrocarbures liquides réfrigérés — Mesurage statique — Procédure de calcul

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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.

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.

International Standard ISO 6578 was prepared by Technical Committee ISO/TC 28, *Petroleum products and lubricants*.

Annexes A to H form an integral part of this International Standard.

Introduction

Storage and transport of large quantities of refrigerated hydrocarbon liquids [e.g. liquefied natural gases (LNG) and liquefied petroleum gases (LPG)] is now common practice. Existing standards for the measurement of petroleum products are either not applicable to, or in some cases inadequate for, these products at low temperatures and, for these products, such standards shall be replaced or modified by the procedures in this International Standard.

Accurate measurement is essential in the sale, purchase and handling of refrigerated hydrocarbon liquids. Custody transfer agreements call for the standardization of static measurement procedures, and it is recommended that quantities be expressed in mass or energy units. It is recognized that other units are currently used for LPG transfers, but these are not covered in this International Standard.

Although the principles of calculating the quantity of a static refrigerated hydrocarbon liquid are basically similar to those for petroleum liquids at ambient temperatures, there are differences caused by the low temperature and the physical properties of refrigerated hydrocarbons. These include the following:

a) The liquid product is at or near a temperature at which bubbles of vapour are first formed within the liquid (bubble point). In a tank containing refrigerated liquid there will always be a small inward flow of heat through the insulation, which will cause a continuous vaporization of the product. The vapour will contain a higher concentration of more volatile constituents than the liquid. To avoid over-pressure, this vapour is vented from the tank and can be compressed, cooled and re-liquefied for re-introduction into the tank.

b) When a liquid product is transferred from one tank to another, additional heat inflow will occur in the pipeline and also from work done by the pump, causing additional evaporation in the receiving tank.

c) For custody transfers from a supply to a receiving tank, it is normal practice to provide a vapour return line linking the tanks to avoid displacement of vapour to the atmosphere. Build-up of pressure in the interlinked system is avoided by re-liquefaction.

d) After a partial filling, stratification into different temperature and density layers may occur in the liquid contents of a tank. Therefore, a number of temperature measuring points and a special sampling system may be necessary. If the filling operation is such as to ensure mixing, these needs may be reduced.

e) There is considerable evidence that large temperature gradients exist in the vapour space of any tank containing a refrigerated hydrocarbon liquid. These gradients may not be linear. Suitable compensation (physical or by calculation) must be made if the reading of the level-measuring device is affected by differential contraction of the level-sensor suspension.

f) Refrigerated hydrocarbon liquids have large temperature coefficients of volumetric expansion and approximate values are given below:

— propane	0,20 %/°C
— methane	0,35 %/°C.

It is very strongly emphasised that errors in temperature measurement can account for the major part of the error in quantitative measurement and the greatest care is therefore needed in the selection and use of temperature measuring equipment.

This International Standard is applicable to the measurement of refrigerated liquids contained in land storage tanks and in ships' tanks when the liquids are fully refrigerated at a vapour pressure near to atmospheric pressure.

However, it is not intended that this International Standard be applied retroactively to existing business contracts, nor should it be applied if it is in conflict with government regulations.

No recommendations are given for the measurement of small parcels of refrigerated liquids, which are directly weighed.

Calculation procedures for refrigerated hydrocarbon liquids consisting predominantly of ethane or ethylene, or for partially refrigerated hydrocarbon liquids at pressures substantially above atmospheric, are not included. Consideration should be given to their inclusion in a subsequent revision, as and when more reliable data become available.

In order to implement the detailed recommendations given in this International Standard, it is essential that personnel responsible for the measurement procedures have the necessary experience and skill. At all times, scrupulous attention must be given to detail.

NOTE — Use of units:

a) Temperature — Celsius temperature is used in connection with the measurement and transport of refrigerated gases and has been used in general in this International Standard; however, in some calculations the thermodynamic, i.e. kelvin, temperature scale must be used. For accurate conversion, 273,15 K ≡ 0 °C should be used, but in the examples given here 273 K ≡ 0 °C is sufficiently accurate.

b) Pressure — The pascal (Pa) is used as the unit of pressure in this standard, but the bar is given as an alternative unit. The bar may be substituted in calculations; the conversion 1 bar = 100 kPa should be used.

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Refrigerated hydrocarbon liquids — Static measurement — Calculation procedure

1 Scope

1.1 This International Standard specifies the calculations to be made to adjust the volume of a refrigerated hydrocarbon liquid, such as LPG or LNG, from the conditions at measurement to the equivalent volume of liquid or vapour at a standard temperature and pressure, or to the equivalent mass or energy (calorific content). It applies to quantities of refrigerated hydrocarbon liquids stored in or transferred to or from tanks and measured under static storage conditions by tank gauges.

1.2 Using these procedures, the final quantity shall be expressed in terms of the following:

a) mass (see the note);

b) energy (calorific content);

c) equivalent volume of vapour under standard conditions.

NOTE — The current practice for measurement of LPG is by apparent mass in air.

The factors in table 1 may be used to convert mass into apparent mass in air.

Table 1

Density at 15 °C kg/m^3	Factor
500,0 to 519,1	0,997 75
519,2 to 542,1	0,997 85
542,2 to 567,3	0,997 95
567,4 to 595,0	0,998 05
595,1 to 625,5	0,998 15
625,6 to 659,3	0,998 25

1.3 If it is required to express the volume of liquid at a standard temperature, the procedures and correlations to determine such quantities are given in clause 4. The standard reference temperature for petroleum products is 15 °C (see ISO 5024), but references are made to calculations involving other widely used reference temperatures, i.e. 20 °C.

1.4 If, for quantity calculations, the product density or the calorific value is required, this shall be either determined directly or calculated from the product composition analysis. The procedures for these subsidiary calculations are given in clauses 8 and 9.

1.5 The mandatory basic data and source references used in the calculation procedures are given in annexes A to F.

2 Normative references

The following standards contain provisions which, through reference in this text, constitute provisions of this International Standard. At the time of publication, the editions indicated were valid. All standards are subject to revision, and parties to agreements based on this International Standard are encouraged to investigate the possibility of applying the most recent editions of the standards indicated below. Members of IEC and ISO maintain registers of currently valid International Standards.

ISO 91-1 : 1982, *Petroleum measurement tables — Part 1: Tables based on reference temperatures of* 15 °C *and* 60 °F.

ISO 91-2 : 1991, *Petroleum measurement tables — Part 2: Tables based on reference temperatures of* 20 °C.

ISO 3993 : 1984, *Liquefied petroleum gas and light hydrocarbons — Determination of density or relative density — Pressure hydrometer method.*

ISO 5024 : 1976, *Petroleum liquids and gases — Measurement — Standard reference conditions.*

3 Definitions and symbols

3.1 Definitions

For the purposes of this International Standard, the following definitions shall apply. Definitions are given for those terms which have particular relevance in calculation procedures used for refrigerated hydrocarbon liquids.[1]

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[1] An International Standard (ISO 4273) dealing with terms relating to petroleum measurement is to be published.

3.1.1 refrigerated hydrocarbon liquids: Liquids composed predominantly of hydrocarbons, which are stored in a fully refrigerated condition at pressures near atmospheric.

3.1.2 liquefied natural gases (LNG): Liquids composed predominantly of methane.

3.1.3 liquefied petroleum gases (LPG): Liquids composed predominantly of any of the following hydrocarbons or mixtures thereof: propane, propene, butanes and butene.

3.1.4 gross calorific value (specific energy) on mass basis: The number of heat units generated when unit mass of a product in the vapour phase at standard temperature and pressure is burned completely in dry air. The gaseous products of combustion are brought to the same standard conditions of temperature and pressure but the water produced is condensed to liquid in equilibrium with water vapour.

3.1.5 gross calorific value (specific energy) on volume basis: The number of heat units generated when unit volume of a product in the vapour phase at standard temperature and pressure is burned completely in dry air. The gaseous products of combustion are brought to the same standard conditions of temperature and pressure but the water produced is condensed to liquid in equilibrium with water vapour.

3.1.6 orthobaric density: The mass of the liquid occupying unit volume at a given temperature, the liquid being in equilibrium with its vapour.

3.1.7 densitometer: An instrument for measuring density.

3.1.8 volume basis (ideal): A volume calculated on the basis that the vapour behaves like an ideal gas.

3.1.9 volume basis (real): Volume calculated on the basis that the vapour behaves like a super-compressible gas.

3.1.10 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 calculated from the ideal gas law.

3.2 Symbols

The following symbols are defined here for use in this International Standard, but additionally some symbols are given a more restricted meaning when used in some equations. The restricted meaning is then given after the equations.

$H_{\mathrm{s},m,i}$ is the gross (superior) calorific value on a mass basis, in megajoules per kilogram, of component i (see annex D);

$H_{\mathrm{s},m}$ is the gross (superior) calorific value on a mass basis, in megajoules per kilogram, of the liquid;

$H_{\mathrm{s},V,i}$ is the gross (superior) calorific value on a volume basis (ideal), in megajoules per cubic metre, of component i (see annex D);

$H_{\mathrm{s,vol}}$ is the gross (superior) calorific value on a volume basis, in megajoules per cubic metre, of the vapour at the appropriate standard temperature and pressure;

m is the mass, in kilograms, of product transferred, i.e. liquid plus vapour;

m_{liq} is the mass, in kilograms, of liquid;

M_i is the molecular mass, in kilograms per kilomole, of component i (see annexes E and G);

M_{mix} is the relative molecular mass, in kilograms per kilomole, of the vapour mixture;

P_{s} is the standard reference pressure, i.e. 101,325 kPa (1,013 25 bar);

P_{vap} is the pressure, in kilopascals (bars), of the vapour in the container;

Q is the net energy, in megajoules, transferred, based on gross calorific value;

Q_{liq} is the energy (calorific) content, in megajoules, of the liquid;

t is the temperature, in degrees Celsius, of the liquid;

T_{s} is the standard reference temperature, i.e. 288,15 K (15 °C);

T_{vap} is the temperature, in kelvins, of the vapour in the container;

V_i is the molar volume, in cubic metres per kilomole, of component i, as a liquid at temperature t °C;

V_{liq} is the volume, in cubic metres, of the liquid at temperature t;

V_{m} is the ideal gaseous molar volume, in cubic metres per kilomole, at standard conditions of pressure and temperature:

i.e. 22,413 8 $\mathrm{m^3/kmol}$ at P_{s} and 273,15 K (0 °C);
23,644 7 $\mathrm{m^3/kmol}$ at P_{s} and T_{s};

V_{vap} is the vapour volume, in cubic metres, in the container;

x_i ; x_j are the mole fractions of the components i and j, respectively;

x_1 is the mole fraction of methane in the LNG;

x_2 is the mole fraction of nitrogen in the LNG;

Z_i is the compressibility factor for component i at the required pressure and temperature;

Z_{mix} is the compressibility factor for the vapour mixture under known conditions of temperature and pressure;

ϱ_t is the density, in kilograms per cubic metre, of the liquid at temperature t.

Additional subscripts: F and I indicate, respectively, the final and initial measurements or product properties in either of the two containers used for a transfer.

NOTE — Other units may be used for the calculations in this International Standard, provided that they are dimensionally consistent, but vapour temperature and pressure should be expressed in absolute units.

4 Volume of LPG at standard temperature

The procedure for converting the volume of refrigerated LPG to its equivalent volume at a standard temperature and corresponding equilibrium pressure includes the following aspects:

a) Very large factors may have to be applied for the correction of observed density to density at standard temperature, e.g. a correction for the effect of a temperature difference of 60 °C may be necessary for refrigerated propane. Provided that the LPG does not contain more than 20 % of unsaturated hydrocarbons the correction tables referred to in ISO 91 shall be used for volume corrections. However, the tables for this density range are those retained from the 1952 edition of the API-ASTM-IP Petroleum Measurement Tables (see sub-clause 3.4 of ISO 91-1 : 1982). If the LPG contains 20 % or more of unsaturated hydrocarbons, the density shall be calculated using the method given in clause 8.

b) The equivalent liquid content in the vapour space of a container holding refrigerated LPG is significantly less than if the tank and contents are at ambient temperature. Therefore, any error in accounting for the equivalent liquid content in the vapour space will be of lesser significance.

NOTES

1 The following examples illustrate the magnitude of errors that can be introduced by using the tables referred to in ISO 91.

a) Pure butene or propene: the maximum error will be approximately 2 % for a correction from −60 °C to +20 °C;

b) Mixtures containing approximately 20 % of unsaturated hydrocarbons: a typical error will be approximately 0,1 % for a temperature difference of 20 °C.

2 A condition in which a liquid has a vapour pressure significantly higher than atmospheric pressure at a standard temperature of 15 °C (or 20 °C or 60 °F) can only be considered as a pseudo-condition, and the volume of the liquid in this condition may be used only when convenient in a procedure for obtaining the density at refrigerated temperatures by means of pressure hydrometer measurement at ambient conditions (see ISO 3993).

5 Mass

5.1 Mass of liquid phase

5.1.1 Calculate the mass of liquid (m_{liq}), in kilograms, using the equation

$$m_{liq} = V_{liq}\,\varrho \qquad \dots (1)$$

where V_{liq} and ϱ are for the same value of the temperature t.

EXAMPLE

Measured volume of liquid LNG in a container = 45 550 m^3 at a temperature of −163,5 °C.

Calculated density at −163,5 °C = 468,3 kg/m^3

Mass of LNG (m_{liq}) = 45 550 × 468,3 kg
= 21,33 × 10^6 kg or 21,33 × 10^3 t

5.1.2 The density at a specified temperature shall be measured using either a pressure hydrometer (LPG) or a suitable densitometer, or shall be calculated from a composition analysis (see clause 8)

5.1.3 If the actual temperature t_2 at which the density is measured does not differ by more than 5 °C from the temperature t_1 of the main bulk of liquid in the container, then the observed density may be corrected to the required bulk temperature by means of the equation

$$\varrho_{t,1} = \varrho_{t,2} + F(t_2 - t_1) \qquad \dots (2)$$

where

$\varrho_{t,1}$ and $\varrho_{t,2}$ are the densities at temperatures t_1 and t_2 respectively;

F is the density correction factor applicable to the particular liquid. The units of F shall be compatible with the units of ϱ, e.g. when ϱ is expressed in kilograms per cubic metre, F is expressed in kg/(m^3·°C).

Product	F kg/(m^3·°C)
LNG [>80 % (m/m) methane]	1,4
Liquid propanes [>60 % (m/m) propane]	1,2
Liquid butanes [>60 % (m/m) butane]	1,1

EXAMPLE

The density of the LNG is 464,8 kg/m^3 at t_2 = −161,0 °C. What is the density of the LNG at −163,5 °C ?

Substituting into equation (2) gives

$$\begin{aligned}\varrho_{t,1} &= 464,8 + 1,4[-161,0 - (-163,5)]\\ &= 464,8 + 3,5\\ &= 468,3 \text{ kg/m}^3\end{aligned}$$

5.1.4 The density of refrigerated LPG may be determined at the standard temperature of 15 °C (or 20 °C or 60 °F) by use of the pressure hydrometer method (see ISO 3993).

The liquid sample drawn into a suitable container is allowed to approach ambient temperature under pressure, without loss of vapour, before it is introduced into the hydrometer cylinder.

5.2 Correction for vapour phase

5.2.1 When a quantity of refrigerated hydrocarbon liquid is transferred, it will be necessary to make a correction for the mass of vapour occupying the volume into which, or from which, the liquid is transferred.

Assuming that all measurements have been made under liquid equlibrium conditions, the following equation can be applied to measurements made in either the delivery or the receiving container.

Mass transferred = Final mass − Initial mass

$$\therefore\ m = \left[V_{\text{liq,F}}\varrho_{\text{F}} + V_{\text{vap,F}} \times \frac{T_{\text{s}}}{T_{\text{vap,F}}} \times \frac{P_{\text{vap,F}}}{P_{\text{s}}} \times \frac{M_{\text{mix,F}}}{V_{\text{m}}Z_{\text{mix,F}}}\right] - \\ - \left[V_{\text{liq,I}}\varrho_{\text{I}} + V_{\text{vap,I}} \times \frac{T_{\text{s}}}{T_{\text{vap,I}}} \times \frac{P_{\text{vap,I}}}{P_{\text{s}}} \times \frac{M_{\text{mix,I}}}{V_{\text{m}}Z_{\text{mix,I}}}\right] \quad \ldots (3)$$

where V_{liq} and ϱ are at the storage temperature t.

If it is impractical to measure the density of the liquid contents of a tank, ϱ_{F} and ϱ_{I} cannot be determined. By using the measured density of the liquid being transferred, however, the simplified equation (3a) can be employed to calculate the mass of product transferred.

$$m = V_{\text{liq}}\varrho - \left(V_{\text{liq}} \times \frac{T_{\text{s}}}{T_{\text{vap,F}}} \times \frac{P_{\text{vap,F}}}{P_{\text{s}}} \times \frac{M_{\text{mix,F}}}{V_{\text{m}}Z_{\text{mix,F}}}\right) \quad \ldots (3a)$$

where

$V_{\text{liq}} = V_{\text{F}} - V_{\text{I}}$ (i.e. the volume of liquid transferred);

ϱ is the average density of the liquid which is transferred.

For a receiving tank which does not already contain hydrocarbon liquid or vapour, equation (3) becomes

$$m = V_{\text{liq,F}}\varrho + \left(V_{\text{vap,F}} \times \frac{T_{\text{s}}}{T_{\text{vap}}} \times \frac{P_{\text{vap}}}{P_{\text{s}}} \times \frac{M_{\text{mix}}}{V_{\text{m}}Z_{\text{mix}}}\right) \quad \ldots (3b)$$

NOTES

1 If the vapour space is negligibly small in comparison with the liquid volume or the liquid volume is negligibly small in comparison with the vapour space in the initial or final condition in the tanks, the simplified equation (3a) may be used in practice.

2 Because the mass of vapour is small compared with the mass of liquid transferred, the accurate knowledge of vapour composition and the use of a compressibility factor are not essential and the ideal gaseous molar volume may be used without correction, and typical values may be used for the temperature and pressure of the vapour space (T_{vap}, P_{vap}) and for the molecular mass and compressibility factor of the vapour mixture (M_{mix}, Z_{mix}).

3 For measurements in a receiving container, equation (3a) is strictly valid only if the temperature of the incoming liquid is the same as that already contained in the tank. The error involved in this assumption is at a maximum when equal volumes of liquid are involved and is then of the order of 0,004 % per kelvin for LNG.

EXAMPLE 1

LNG transfer from a container

Volume of liquid LNG transferred at temperature t	= 45 550 m^3
Measured temperature of liquid, t	= −163,5 °C
Liquid density at −163,5 °C	= 468,3 kg/m^3
Average temperature of vapour after transfer	= −118 °C = 155 K
Pressure of vapour after transfer	= 110 kPa
It may be assumed that the molecular mass of the vapour mixture is that of pure methane (obtained from annex B)	= 16,042 6 kg/mol

The compressibility factor for the vapour can be taken as unity, with a resultant error of less than 0,05 %.

$$m = \left[(45\,550 \times 468{,}3) - \\ - \left(45\,550 \times \frac{288}{155} \times \frac{110}{101{,}3} \times \frac{16{,}042\,6}{23{,}644\,7}\right)\right]$$

$$= 21\,331\,065 - 62\,355$$

$$= 21\,269 \times 10^3 \text{ kg or } 21\,269 \text{ t}$$

EXAMPLE 2

LPG transfer from a container

Calculate the mass of LPG transferred from a container under the following conditions:

	Initial	**Final**
Volume of liquid in container at 15 °C (m^3)	45 550	850
Liquid density at 15 °C (kg/m^3)	507	507
Vapour space in container (m^3)	950	40 000
Temperature of vapour in container (K)	233	250
Pressure in container vapour space (bar)	1,08	1,12

It may be assumed that the molecular mass of the vapour mixture is the same as that of the liquid and that the compressibility factor is unity, i.e. M_{mix} = 44,153 kg/kmol

Substituting into equation (3) gives:

$$m = \left[(45\ 550 \times 507) + \left(950 \times \frac{288}{233} \times \frac{1{,}08}{1{,}013} \times \frac{44{,}153}{23{,}644\ 7} \right) \right] - \left[(850 \times 507) + \left(40\ 000 \times \frac{288}{250} \times \frac{1{,}12}{1{,}013} \times \frac{44{,}153}{23{,}644\ 7} \right) \right]$$

$$= (23\ 093\ 850 + 2\ 338) - (430\ 950 + 95\ 137)$$

$$= 22\ 570 \times 10^3 \text{ kg or } 22\ 570 \text{ tonnes}$$

5.2.2 Similarly, if the energy measurements are required for stock purposes, take into consideration the liquid equivalent of the vapour in the total ullage space.

6 Energy content (calorific content)

6.1 Calculate the energy content of the liquid using the equation

$$Q_{\text{liq}} = m_{\text{liq}} H_{\text{s},m} \qquad \ldots (4)$$

6.2 When a quantity of refrigerated hydrocarbon liquid is transferred, it will be necessary to make a correction for the calorific content of the vapour occupying the volume into which, or from which, the liquid is transferred.

Assuming that all measurements have been made under liquid equilibrium conditions, the following equation applies to measurements made in either the delivery or the receiving container.

Energy delivered = Final energy content − Initial energy content

$$\therefore Q = \left[V_{\text{liq,F}} \varrho_{\text{F}} H_{\text{s},m,\text{F}} + V_{\text{vap,F}} \times \frac{T_{\text{s}}}{T_{\text{vap,F}}} \times \frac{P_{\text{vap,F}}}{P_{\text{s}}} \times H_{\text{s,vol,F}} \right] - \left[V_{\text{liq,I}} \varrho_{\text{I}} H_{\text{s},m,\text{I}} + V_{\text{vap,I}} \times \frac{T_{\text{s}}}{T_{\text{vap,I}}} \times \frac{P_{\text{vap,I}}}{P_{\text{s}}} \times H_{\text{s,vol,I}} \right] \qquad \ldots (5)$$

where

$H_{\text{s,vol}} = \dfrac{M_{\text{mix}}}{V_{\text{m}} Z_{\text{mix}}} \times H_{\text{s},m}$ = the gross calorific value on volume basis, in megajoules per cubic metre, of the vapour at the appropriate standard temperature and pressure.

If it is impractical to measure the density of the liquid contents of a tank, ϱ_{F} and ϱ_{I} cannot be determined. By using the measured density of the liquid being transferred, however, the simplified equation (5a) may be employed to calculate the net energy delivered or received.

$$Q = V_{\text{liq}} \varrho H_{\text{s},m} - \left(V_{\text{liq}} \times \frac{T_{\text{s}}}{T_{\text{vap}}} \times \frac{P_{\text{vap}}}{P_{\text{s}}} \times H_{\text{s,vol}} \right) \ldots (5\text{a})$$

where

$V_{\text{liq}} = V_{\text{liq,F}} - V_{\text{liq,I}}$ (i.e. the volume of liquid transferred);

ϱ is the average density of the liquid which is transferred.

For a receiving tank which does not already contain hydrocarbon liquid or vapour, equation (5) becomes

$$Q = V_{\text{liq}} \varrho H_{\text{s},m} + \left(V_{\text{vap,F}} \times \frac{T_{\text{s}}}{T_{\text{vap}}} \times \frac{P_{\text{vap}}}{P_{\text{s}}} \times H_{\text{s,vol}} \right) \qquad \ldots (5\text{b})$$

NOTE — See 5.2.1, notes 1, 2 and 3, but for "equation (3a)" read "equation (5a)".

EXAMPLE 1

LNG transfer from a container

Volume of liquid LNG transferred at temperature t	= 45 550 m^3
Liquid temperature, t	= −163,5 °C
Liquid density at −163,5 °C	= 468,3 kg/m^3
Average temperature of vapour after transfer	= −118 °C = 155 K
Pressure of vapour after transfer	= 110 kPa
Gross calorific value on mass basis of the liquid using example 1 given in 9.2, i.e. $H_{\text{s,m}}$	= 54,216 MJ/kg
It may be assumed that the gross calorific value on volume basis for the vapour mixture is that for pure methane at 101,325 kPa and 15 °C (see annex D)	= 37,696 MJ/m^3

The compressibility factor for the vapour is assumed to be unity, and the resultant error will be less than 0,005 %.

$$Q = (45\ 550 \times 468{,}3 \times 54{,}216) - \left(45\ 550 \times \frac{288}{155} \times \frac{110}{101{,}3} \times 37{,}696 \right)$$

$$= (1\ 156{,}848 \times 10^6) - 3{,}46 \times 10^6)$$

$$Q = 1\ 153{,}0 \times 10^6 \text{ MJ}$$

EXAMPLE 2

LPG transfer from a container

Calculate the calorific content of the LPG transferred from a container under the following conditions:

	Initial	Final
Volume of liquid in container at 15 °C (m³)	45 550	850
Liquid density at 15 °C (kg/m³)	507	507
Vapour space in container (m³)	950	40 000
Temperature of vapour in container (K)	233	250
Pressure in container vapour space (bar)	1,08	1,12

Gross calorific value on mass basis for the liquid, using example 2 given in 9.2, i.e. $H_{s,m}$ = 50,384 MJ/kg.

It may be assumed that the gross calorific value on volume basis for the vapour mixture is that for pure propane at 1,013 25 bar and 15 °C (see annex D), i.e. $H_{s,vol}$ = 93,973 MJ/m³.

Substituting into equation (5) gives:

$$Q = \left[(45\,550 \times 507 \times 50{,}384) + \right.$$

$$\left. + \left(950 \times \frac{288}{233} \times \frac{1{,}08}{1{,}013} \times 93{,}973\right) \right] -$$

$$- \left[(850 \times 507 \times 50{,}384) + \right.$$

$$\left. + \left(40\,000 \times \frac{288}{250} \times \frac{1{,}12}{1{,}013} \times 93{,}973\right) \right]$$

$$= (1\,163{,}56 \times 10^6 + 0{,}12 \times 10^6) -$$

$$- (21{,}72 \times 10^6 + 4{,}79 \times 10^6)$$

$$= 1\,137{,}2 \times 10^6 \text{ MJ}$$

6.3 Similarly, where measurements are required for stock purposes, it will be necessary to take into consideration the energy content of the vapour in the total ullage space.

7 Inter-conversion of liquid mass and vapour volume at standard conditions

7.1 The inter-relationship between a mass of liquid and the volume it occupies as a vapour at standard conditions is given by the equation

$$V_{vap} = \frac{m_{liq} V_m Z_{mix}}{M_{mix}} \qquad \ldots (6a)$$

or

$$m_{liq} = \frac{V_{vap} M_{mix}}{V_m Z_{mix}} \qquad \ldots (6b)$$

where

V_{vap} is expressed at the required standard conditions;

$$M_{mix} = \sum x_i M_i \qquad \ldots (6c)$$

7.2 The compressibility factor which is commonly used to calculate the volume of a vapour mixture at standard conditions is given by the equation

$$Z_{mix} = 1 - \left[\sum x_i (1 - Z_i)^{1/2}\right]^2 \qquad \ldots (7)$$

Values of Z_i, as well as those of the molecular mass M_i and the expression $(1 - Z_i)^{1/2}$ for the various components, are given in annex E.

EXAMPLE 1

Calculate the compressibility factor at standard atmospheric pressure and 15 °C for a vapour having the following composition:

CH_4	90,0 % (mol/mol)
C_2H_6	4,9 % (mol/mol)
C_3H_8	2,9 % (mol/mol)
n-C_4H_4	1,3 % (mol/mol)
i-C_4H_{10}	0,4 % (mol/mol)
n-C_5H_{12}	0,1 % (mol/mol)
N_2	0,4 % (mol/mol)

Table 2

Component (see annex F)	M_i	Mole fraction x_i	x_iM_i	$(1-Z_i)^{1/2}$	$x_i(1-Z_i)^{1/2}$
CH_4	16,042 6	0,900	14,438 3	0,044 7	0,040 2
C_2H_6	30,069 4	0,049	1,473 4	0,092 7	0,004 5
C_3H_8	44,096 2	0,029	1,278 8	0,139 3	0,004 0
n-C_4H_{10}	58,123 0	0,013	0,755 6	0,191 3	0,002 5
i-C_4H_{10}	58,123 0	0,004	0,232 5	0,184 7	0,000 7
n-C_5H_{12}	72,149 8	0,001	0,072 1	0,236 6	0,000 2
N_2	28,013 4	0,004	0,112 1	0,173 2	0,000 1
Σ	—	1,000	18,362 8	—	0,052 2

$$Z_{mix} = 1 - \left[\sum x_i (1 - Z)^{1/2}\right]^2$$

$$= 1 - (0{,}052\,2)^2$$

$$= 0{,}997\,3$$

EXAMPLE 2

Calculate the equivalent volume of vapour at standard conditions (1,013 25 bar and 15 °C) corresponding to a mass of 21 331 t of LNG.

Assume the molecular mass M_{mix} = 18,362 8

Assume the compressibility factor Z_{mix} = 0,997 3

V_m = 23,644 7 m³/kmol at 101,325 kPa (1,013 25 bar) and 15 °C (see 3.2)

$$V_{vap} = 21\,331 \times 10^3 \times 23{,}644\,7 \times \frac{0{,}997\,3}{18{,}362\,8}$$

$$= 27{,}393 \times 10^6 \text{ m}^3 \text{ at } 101{,}325 \text{ kPa } (1{,}013\,25 \text{ bar}) \text{ and } 15\ °\text{C}$$

8 Calculation of liquid density from composition

8.1 General

The density of refrigerated hydrocarbon liquids can be calculated from the equation

$$\varrho_t = \frac{\sum x_i M_i}{\sum (x_i V_i) - V_c} \qquad \ldots (8)$$

where V_c is the reduction in volume, in cubic metres per kilomole, on mixing the components at t °C (see notes to 8.2).

8.2 LPG — propane and butane mixtures

For liquids at temperatures between +30 and −60 °C, V_i is given by the equations

$$V_i = \frac{M_i}{A - Bt - [C/(E - t)]} \qquad \ldots (9)$$

and

$$V_t = \sum V_i \qquad \ldots (9a)$$

where

A, B, C and E are the constants for each component, given in annex A;

V_t is the molar volume, in cubic metres per kilomole, of the liquid at its temperature t °C.

NOTES

1 The reduction in volume on mixing components is ignored in equation (9). An alternative equation for calculating V_t which includes a correction for reduction in volume on mixing components is given in annex G and may be used if agreed between the interested parties.

2 Molar volumes at the various reference temperatures (15 °C, 20 °C and 60 °F) are given in annex A for the components of the liquids. These may alternatively be used in equation (9) to calculate the liquid densities at the reference temperature if agreed between the interested parties.

3 If calculations involving density determined using more than one of these alternatives are compared, there will be differences between the final results. The magnitude of the differences will vary with changes in molar composition.

8.3 LNG — methane or mixtures having methane as main constituent

For liquids at temperatures between −180 °C and −140 °C, V_i can be calculated from the basic data given in annex B.

For an LNG mixture having an average molecular mass of 20,0 kg/kmol, or less, and with less than 5 % molar of nitrogen, 5 % molar of *n*-butane plus *iso*-butane, 1 % molar of all pentanes plus heavier hydrocarbons, and traces of oxygen, V_c is given by the equation

$$V_c = \left[k_1 + (k_2 - k_1) \frac{x_2}{0{,}042\,5} \right] x_1 \qquad \ldots (10)$$

where

k_1 is the correction factor, in cubic metres per kilomole, due to the presence of hydrocarbons and based on the average molecular mass and temperature of the mixture as given in table C.1 of annex C;

k_2 is the correction factor, in cubic metres per kilomole, due to the presence of nitrogen and based on the average molecular mass and temperature of the mixture as given in table C.2 of annex C.

NOTE — This method of calculating V_c is the best available at the time of publication, and may be amended in the light of work in progress.

EXAMPLE 1

Density calculation for LNG having the same composition as example 1 in 7.2. The density is required at −163,5 °C.

Table 3

Component (see annex F)	M_i	**Mole fraction** x_i	$x_i M_i$	V_i at −163,5 °C (see the note)	$x_i V_i$
CH_4	16,042 6	0,900	14,438 3	0,037 695	0,033 926
C_2H_6	30,069 4	0,049	1,473 4	0,047 649	0,002 335
C_3H_8	44,096 2	0,029	1,278 8	0,062 181	0,001 803
n-C_4H_{10}	58,123 0	0,013	0,755 6	0,076 541	0,000 995
i-C_4H_{10}	58,123 0	0,004	0,232 5	0,078 001	0,000 312
n-C_5H_{12}	72,149 8	0,001	0,072 1	0,091 342	0,000 091
N_2	28,013 4	0,004	0,112 1	0,044 936	0,000 180
Σ	—	1,000	18,362 8	—	0,039 642

Average molecular mass = 18,362 8

Factor $k_1 = 0{,}436 \times 10^{-3}$ obtained by interpolation in table C.1 of annex C.

Factor $k_2 = 0{,}641 \times 10^{-3}$ obtained by interpolation in table C.2 of annex C.

$$\therefore V_c = \left[0{,}000\,436 + (0{,}000\,641 - 0{,}000\,436) \times \times \frac{0{,}004}{0{,}042\,5} \right] \times 0{,}9$$

$$= 0{,}000\,41$$

$$\text{Density} = \varrho_t = \frac{\sum x_i M_i}{\sum (x_i V_i) - V_c} = \frac{18{,}362\,8}{(0{,}039\,642 - 0{,}000\,41)}$$

$$= 468{,}1 \text{ kg/m}^3$$

NOTE — These values are obtained by interpolation, between −160 °C and −165 °C, of the data given in annex B.

EXAMPLE 2

Calculate the density at −43 °C of LPG which has the molar composition given in table 4.

Table 4

Component (see annex F)	Mole fraction x_i	M_i	V_i at −43 °C [see equation (9)]	$x_i M_i$	$x_i V_i$
C_2H_6	0,009	30,069 4	0,061 805	0,271	0,000 556
C_3H_8	0,978	44,096 2	0,075 789	43,126	0,074 122
$n\text{-}C_4H_{10}$	0,013	58,123 0	0,090 191	0,756	0,001 172
Σ	1,000	—	—	44,153	0,075 850

$$\text{Density} = \varrho_t = \frac{\sum x_i M_i}{\sum x_i V_i}$$

$$= \frac{44,153}{0,075\ 850}$$

$$= 582,1\ \text{kg/m}^3$$

9 Calculation of calorific value from composition

9.1 Gas volume basis

The gross calorific value, on a gas volume basis, of a mixture may be calculated from the equation

$$H_{\text{s,vol}} = \frac{\sum x_i H_{\text{s},V,i}}{Z_{\text{mix}}} \qquad \dots (11)$$

EXAMPLE

Table 5

Component (see annex F)	x_i	$H_{\text{s},V,i}$ at 1,013 25 bar and 15 °C MJ/kg	$x_i H_{\text{s},V,i}$
CH_4	0,900	37,696	33,926
C_2H_6	0,049	66,035	3,236
C_3H_8	0,029	93,975	2,725
$n\text{-}C_4H_{10}$	0,013	121,782	1,583
$i\text{-}C_4H_{10}$	0,004	121,428	0,486
$n\text{-}C_5H_{12}$	0,001	149,676	0,150
N_2	0,004	0	0,000
Σ	1,000	—	42,106

$Z_{\text{mix}} = 0,997\ 3$ (see 7.2, example 1)

Gross calorific value on gas volume basis $H_{\text{s,vol}}$

$$= \frac{42,106}{0,997\ 3} = 42,22\ \text{MJ/m}^3$$

9.2 Mass basis

The gross calorific value, on a mass basis, of a mixture may be calculated from the equation

$$H_{\text{s},m} = \sum H_{\text{s},m,i} \left[\frac{x_i M_i}{\sum (x_i M_i)} \right] \qquad \dots (12)$$

EXAMPLE 1

Table 6

Component (see annex F)	M_i	x_i	x_iM_i	$\frac{x_iM_i}{\sum (x_iM_i)}$	$H_{s,m,i}$ at 101,3 kPa and 15 °C MJ/kg	$H_{s,m,i} \times \frac{x_iM_i}{\sum (x_iM_i)}$
CH_4	16,042 6	0,900	14,438 3	0,786 3	55,558	43,684
C_2H_6	30,069 4	0,049	1,473 4	0,080 2	51,925	4,166
C_3H_8	44,096 2	0,029	1,278 8	0,069 6	50,389	3,509
n-C_4H_{10}	58,123	0,013	0,755 6	0,041 1	49,541	2,039
i-C_4H_{10}	58,123	0,004	0,232 5	0,012 7	49,397	0,625
n-C_5H_{12}	72,149 8	0,001	0,072 1	0,003 9	49,051	0,193
N_2	28,013 4	0,004	0,112 1	0,006 1	0	0
Σ	—	1,000	18,362 8	1,000 0	—	54,216

Gross calorific value on mass basis of the mixture $H_{s,m}$ = 54,216 MJ/kg.

EXAMPLE 2

Table 7

Component (See annex F)	M_i	x_i	x_iM_i	$\frac{x_iM_i}{\sum (x_iM_i)}$	$H_{s,m,i}$ à 101,3 kPa and 15 °C MJ/kg	$H_{s,m,i} \times \frac{x_iM_i}{\sum (x_iM_i)}$
C_2H_6	30,069 4	0,009	0,271	0,006 1	51,925	0,317
C_3H_8	44,096 2	0,978	43,126	0,976 8	50,389	49,220
n-C_4H_{10}	58,123	0,013	0,756	0,017 1	49,541	0,847
Σ	—	1,000	44,153	1,000 0	—	50,384

Gross calorific value on mass basis of the mixture $H_{s,m}$ = 50,384 MJ/kg.

Annex A
(normative)

Constants for density calculations

[for use in equation (9)]

Table A.1

Component	Molecular mass M_i	Constants				Molar volume, V_i, at the reference temperature m³/kmol		
	kg/kmol	*A*	*B*	*C*	*E*	15 °C	20 °C	60 °C
C_2H_6	30,069 4	499,0	0,99	6 000	66	0,083 992	0,088 464	0,084 452
C_3H_8	44,096 2	575,0	0,97	6 000	129	0,086 872	0,088 104	0,086 940
n-C_4H_{10}	58,123 0	637,6	0,87	7 000	186	0,099 407	0,100 420	0,099 555
i-C_4H_{10}	58,123 0	616,7	0,97	6 000	169	0,103 183	0,104 313	0,103 321
n-C_5H_{12}	72,149 8	676,2	0,87	7 000	231	0,114 366	0,115 215	0,114 455
i-C_5H_{12}	72,149 8	666,6	0,88	6 000	222	0,115 508	0,116 437	0,115 608
n-C_6H_{14}	86,176 6	705,0	0,83	7 000	269	0,129 820	0,130 700	0,129 912
n-C_7H_{16}	100,203 4	731,9	0,85	7 000	301	0,145 646	0,146 551	0,145 743
C_2H_4	28,053 6	502,8	1,09	7 000	44	—	—	—
C_3H_6	42,080 4	601,2	1,02	7 000	126	0,080 520	0,081 884	0,080 692
n-C_4H_8	56,107 2	657,4	0,97	7 000	180	0,093 294	0,094 282	0,093 401

NOTE — The use of these constants in equation (9) should be restricted to LPG mixtures which are either predominantly propane/propylene in the temperature range +30 °C to −60 °C or predominantly butane/butylene in the temperature range +30 °C to −20 °C.

Bibliography

[1] FRANCIS, A.W., Pressure-temperature liquid density relations of pure hydrocarbons, *Industrial and Engineering Chemistry*, **49**, No. 10 (1957).

[2] *API Research Project 44*, Physical Constants of Hydrocarbons, C_1 to C_{10}.

Annex B
(normative)

Orthobaric molar volumes of individual components of LNG

Table B.1

Component (see annex F)	Molecular mass M_i kg/mol	Molar volume V_i, m³/kmol								
		− 180 °C	− 175 °C	− 170 °C	− 165 °C	− 160 °C	− 155 °C	− 150 °C	− 145 °C	− 140 °C
CH_4[3]	16,042 6	0,035 771	0,036 315	0,036 891	0,037 500	0,038 149	0,038 839	0,039 580	0,040 375	0,041 237
C_2H_6[3]	30,069 4	0,046 324	0,046 716	0,047 116	0,047 524	0,047 942	0,048 369	0,048 806	0,049 253	0,049 711
C_3H_8[3]	44,096 2	0,060 731	0,061 164	0,061 602	0,062 046	0,062 497	0,062 953	0,063 417	0,063 887	0,064 364
$n\text{-}C_4H_{10}$[3]	58,123 0	0,074 997	0,075 459	0,075 926	0,076 398	0,076 875	0,077 359	0,077 847	0,078 342	0,078 843
$i\text{-}C_4H_{10}$[3]	58,123 0	0,076 384	0,076 868	0,077 356	0,077 851	0,078 352	0,078 859	0,079 374	0,079 896	0,080 425
$n\text{-}C_5H_{12}$[4]	72,149 8	0,089 498	0,090 016	0,090 536	0,091 058	0,091 583	0,092 111	0,092 642	0,093 177	0,093 715
$i\text{-}C_5H_{12}$[4]	72,149 8	0,089 576	0,090 107	0,090 642	0,091 179	0,091 721	0,092 267	0,092 817	0,093 372	0,093 930
$n\text{-}C_6H_{14}$[4]	86,176 6	0,102 73	0,103 26	0,103 80	0,104 34	0,104 89	0,105 45	0,106 02	0,106 59	0,107 16
N_2[3]	28,013 4	0,038 408	0,039 949	0,041 788	0,044 043	0,047 019	0,051 022	0,055 897	0,061 767	0,069 064
O_2[4]	31,998 8	—	—	0,029 80	0,030 61	0,031 51	0,032 52	0,033 67	—	—

NOTES

1 The exact molar volume at any temperature is obtained by interpolation, assuming exact linearity between adjacent values in the table.

2 The above values of V_i are the best available at the time of publication and may be amended in the light of work in progress.

Bibliography

[3] HAYNES, W.M., HIZA, M.J., and MCCARTY, R.D., Density of LNG for custody transfer, *Proceedings of 5th International Conference on LNG*, Dusseldorf, Germany, F.R., 1977.

[4] KLOSEK, J., and MCKINLEY, C., Densities of liquefied natural gas and of the low molecular weight hydrocarbons, *Proceedings of 1st International Conference on LNG*, 1968.

Annex C
(normative)

Correction factors for volume reduction of LNG mixtures

Table C.1 — Correction factor k_1

Molecular mass of mixture $\sum x_i M_i$	$k_1 \times 10^3$, m^3/kmol								
	− 180 °C	− 175 °C	− 170 °C	− 165 °C	− 160 °C	− 155 °C	− 150 °C	− 145 °C	− 140 °C
16	−0,01	−0,01	−0,01	−0,01	−0,01	−0,01	−0,01	−0,01	−0,01
17	0,13	0,15	0,16	0,18	0,21	0,24	0,28	0,33	0,38
18	0,25	0,29	0,33	0,37	0,41	0,47	0,56	0,66	0,76
19	0,37	0,41	0,45	0,51	0,58	0,67	0,76	0,87	1,01
20	0,47	0,52	0,59	0,67	0,76	0,86	0,98	1,10	1,30
21	0,55	0,62	0,70	0,79	0,89	1,00	1,13	1,29	1,45
22	0,64	0,72	0,81	0,90	1,01	1,17	1,32	1,52	1,71
23	0,72	0,82	0,92	1,02	1,15	1,33	1,53	1,68	1,84
24	0,81	0,92	1,04	1,16	1,30	1,47	1,66	1,87	2,13
25	0,88	1,00	1,12	1,25	1,41	1,58	1,78	2,00	2,27
26	0,95	1,07	1,19	1,33	1,50	1,68	1,89	2,13	2,41
27	1,01	1,13	1,26	1,41	1,58	1,78	1,99	2,24	2,53
28	1,06	1,18	1,32	1,47	1,64	1,84	2,06	2,32	2,62
29	1,11	1,23	1,37	1,54	1,72	1,92	2,15	2,42	2,73
30	1,16	1,29	1,43	1,60	1,79	2,00	2,24	2,51	2,83

Table C.2 — Correction factor k_2

Molecular mass of mixture $\sum x_i M_i$	$k_2 \times 10^3$, m^3/kmol								
	− 180 °C	− 175 °C	− 170 °C	− 165 °C	− 160 °C	− 155 °C	− 150 °C	− 145 °C	− 140 °C
16	0	−0,01	−0,01	−0,01	−0,02	−0,03	−0,04	−0,05	−0,07
17	0,11	0,15	0,21	0,29	0,46	0,68	0,91	1,21	1,60
18	0,26	0,32	0,39	0,53	0,67	0,84	1,05	1,34	1,80
19	0,40	0,47	0,57	0,71	0,88	1,13	1,39	1,76	2,22
20	0,56	0,62	0,71	0,86	1,06	1,33	1,62	2,03	2,45
21	0,67	0,76	0,87	1,01	1,16	1,48	1,85	2,26	2,79
22	0,78	0,90	1,01	1,16	1,27	1,65	2,09	2,51	3,13
23	0,88	1,03	1,15	1,30	1,42	1,85	2,33	2,81	3,49
24	0,98	1,13	1,27	1,45	1,60	2,06	2,58	3,11	3,74
25	1,07	1,22	1,38	1,61	1,89	2,28	2,73	3,29	3,97
26	1,15	1,31	1,50	1,74	2,04	2,44	2,92	3,48	4,19
27	1,22	1,40	1,61	1,87	2,19	2,60	3,10	3,71	4,46
28	1,31	1,50	1,72	1,99	2,33	2,77	3,31	3,95	4,74
29	1,38	1,59	1,83	2,12	2,48	2,95	3,51	4,19	5,03
30	1,47	1,68	1,93	2,24	2,63	3,12	3,72	4,45	5,34

NOTES

1 The exact correction factor at any temperature and molecular mass is obtained by interpolation, assuming exact linearity between adjacent values in the table.

2 The above values of correction factors k_1 and k_2 are the best available at the time of publication and may be amended in the light of work in progress.

3 The above values of correction factors k_1 and k_2 are expressed as the value derived after multiplying by 10^3 to avoid an excessive number of noughts in the table. When applying the factors, a compensating multiplier of 10^{-3} should be entered to reduce the above values to the correct magnitude (see example 1 in 8.3).

Bibliography

[3] HAYNES, W.M., HIZA, M.J., and MCCARTY, R.D., Density of LNG for custody transfer, *Proceedings of 5th International Conference on LNG*, Dusseldorf, Germany, F.R., 1977.

Annex D
(normative)

Gross calorific values for individual components

Table D.1

Component (see annex F)	**Gross calorific value on mass basis** $H_{s,m,i}$ (MJ/kg) at 101,325 kPa (1,013 25 bar) and 15 °C	**Gross calorific value on volume basis (ideal)** $H_{s,V,i}$ (MJ/m^3) at 101,325 kPa (1,013 25 bar) and 15 °C	**Gross calorific value on volume basis (real)** (MJ/m^3) at 101,325 kPa (1,013 25 bar) and 15 °C
CH_4	55,558	37,696	37,772
C_2H_6	51,925	66,035	66,608
C_3H_8	50,389	93,975	95,834
n-C_4H_{10}	49,541	121,782	126,408
i-C_4H_{10}	49,397	121,428	125,715
n-C_5H_{12}	49,051	149,676	158,555
i-C_5H_{12}	48,939	149,336	157,212
n-C_6H_{14}	48,716	177,556	194,795
n-C_7H_{16}	48,475	205,432	237,411
C_2H_4	50,315	59,700	60,070
C_3H_6	48,950	87,120	88,550
C_4H_8 (mean)	48,296	114,61	118,52
H_2S	16,519	23,807	24,038

NOTE — The "ideal" calorific values are used for the calculation of calorific values of mixtures as described in 9.1. The "real" calorific values are listed for convenience when pure gases are involved and are derived from $\frac{H_{s,V,i}}{Z_i}$.

Bibliography

The calorific values in table D.1 are calculated from the standard heats of reaction at 25 °C given in the following publications:

[5] ISO 6976 : 1983, *Natural gas — Calculation of calorific value, density and relative density*.

[6] *API Research Project 44*.

Annex E
(normative)

Relative molecular masses and compressibility factors of individual components

Table E.1

Component (see annex F)	**Relative molecular mass M_i** kg/kmol	**Compressibility factor Z_i** at 101,325 kPa (1,013 25 bar) and 15 °C	$(1 - Z_i)^{1/2}$
CH_4	16,042 6	0,998 0	0,044 7
C_2H_6	30,069 4	0,991 4	0,092 7
C_3H_8	44,096 2	0,980 6	0,139 3
n-C_4H_{10}	58,123 0	0,963 4	0,191 3
i-C_4H_{10}	58,123 0	0,965 9	0,184 7
n-C_5H_{12}	72,149 8	0,944 0	0,236 6
i-C_5H_{12}	72,149 8	0,949 9	0,223 8
n-C_6H_{14}	86,176 6	0,911 5	0,297 5
n-C_7H_{16}	100,203 4	0,865 3	0,367 0
C_2H_4	28,053 6	0,993 9	0,078 10
C_3H_6	42,080 4	0,983 8	0,127 28
C_4H_8 (mean)	56,107 2	0,967 0	0,181 66
N_2	28,013 4	0,999 7	0,017 32
CO_2	44,009 8	0,994 3	0,075 50
H_2S	34,076 0	0,990 4	0,098 0

NOTE — The relative molecular masses are based on that of carbon being 12,011 ± 0,001 and that of hydrogen being 1,007 9 ± 0,000 1.

Bibliography

[7] *API Research Project 44*, Tables 23.2 (1.2001 to 1.2007).

[8] MASON, D.M., and EAKIN, B.E., *Research Bulletin*, No. 32 (1961).

Annex F
(normative)

Chemical names corresponding to chemical formulae used in this International Standard

Table F.1

Chemical name	Formula
Methane	CH_4
Ethane	C_2H_6
Propane	C_3H_8
Butane	$n\text{-}C_4H_{10}$
Isobutane	$i\text{-}C_4H_{10}$
Pentane	$n\text{-}C_5H_{12}$
Isopentane	$i\text{-}C_5H_{12}$
Hexane	$n\text{-}C_6H_{14}$
Isohexane	$i\text{-}C_6H_{14}$
Heptane	$n\text{-}C_7H_{16}$
Ethene	C_2H_4
Propene	C_3H_6
But-1-ene	$n\text{-}C_4H_8$
Nitrogen	N_2
Oxygen	O_2
Carbon dioxide	CO_2
Hydrogen sulfide	H_2S

Annex G
(normative)

Alternative equation for calculating the molar volume and saturated density of LPG mixtures

NOTE — This method is intended for use when agreed between the interested parties.

G.1 Basic equations

$$V_t = V^* V_{\mathrm{R1}}(1 - \omega_{\mathrm{mix}} V_{\mathrm{R2}}) \qquad \ldots (13)$$

$$\varrho_t = \frac{\sum x_i M_i}{V_t} \qquad \ldots (14)$$

$$V_{\mathrm{R1}} = 1 + a(1 - T_{\mathrm{R}})^{1/3} + b(1 - T_{\mathrm{R}})^{2/3} + c(1 - T_{\mathrm{R}}) + d(1 - T_{\mathrm{R}})^{4/3} \qquad \ldots (15)$$

$$V_{\mathrm{R2}} = \frac{e + fT_{\mathrm{R}} + gT_{\mathrm{R}}^2 + hT_{\mathrm{R}}^3}{T_{\mathrm{R}} - 1{,}000\ 01} \qquad \ldots (16)$$

$$T_{\mathrm{R}} = \frac{T}{T_{\mathrm{c,mix}}} \qquad \ldots (17)$$

where

V_t is the molar volume, in cubic metres per kilomole, of the LPG mixture at temperature t °C;

V^* is the characteristic volume, in cubic metres per kilomole (see annex H);

ω_{mix} is the acentric factor for the mixture $= \sum x_i \omega_i$

where ω_i is the acentric factor for component i (see annex H);

V_{R1} is the corresponding-states function for normal fluids (see reference [9]);

V_{R2} is the deviation function for new correlation;

$T_{\mathrm{c},i}$ is the critical temperature, in kelvins, of component i (see annex H);

$T_{\mathrm{c,mix}}$ is the critical temperature, in kelvins, of the mixture;

T is the temperature, in kelvins, of the liquid ($T = t + 273{,}15$);

$$\left.\begin{aligned} a &= -1{,}528\ 16 \\ b &= 1{,}439\ 07 \\ c &= -0{,}814\ 46 \\ d &= 0{,}190\ 454 \end{aligned}\right\} \text{ are constants for equation (15)}$$

$$\left.\begin{aligned} e &= -0{,}296\ 123 \\ f &= 0{,}386\ 914 \\ g &= -0{,}042\ 725\ 8 \\ h &= -0{,}048\ 064\ 5 \end{aligned}\right\} \text{ are constants for equation (16)}$$

ϱ_t, M_i and x_i are as defined in 3.2.

G.2 Equations for mixtures

$$\sum x_i M_i = \sum_{i=1}^{n} x_i M_i \qquad \ldots (18)$$

$$\sum x_i \omega_i = \sum_{i=1}^{n} x_i \omega_i \qquad \ldots (19)$$

$$V_{\mathrm{mix}}^* = \frac{1}{4}\left[\sum_{i=1}^{n} x_i V_i^* + 3\left(\sum_{i=1}^{n} x_i V_i^{*2/3}\right)\left(\sum_{i=1}^{n} x_i V_i^{*1/3}\right)\right] \qquad \ldots (20)$$

$$T_{\mathrm{c,mix}} = \frac{\displaystyle\sum_{i=1}^{n}\sum_{j=1}^{n} x_i x_j V_{ij}^* T_{\mathrm{c},ij}}{V_{\mathrm{mix}}^*} \qquad \ldots (21)$$

where

$$V_{ij}^* T_{\mathrm{c},ij} = (V_i^* T_{\mathrm{c},i} V_j^* T_{\mathrm{c},j})^{1/2} \qquad \ldots (22)$$

V_{mix}^* is the characteristic volume of the mixture, in cubic metres per kilomole.

Bibliography

[9] HANKINSON, R.W., and THOMSON, G.H., COSTALD (Corresponding states liquid density) equation, *Hydrocarbon Processing*, Sept. 1979.

G.3 Example (see also example 2 in 8.3)

Calculate the density at −43 °C of LPG which has a molar composition given in table G.1 :

Table G.1

Component (see annex F)	Mole fraction x_i	M_i	$x_i M_i$	V_i^* (see annex H)	$x_i V_i^*$	$V_i^{*1/3}$	$x_i V_i^{*1/3}$	$V_i^{*2/3}$	$x_i V_i^{*2/3}$	$T_{c,i}$ (see annex H)	ω_i (see annex H)	$x_i \omega_i$
C_2H_6	0,009	30,069 4	0,271	0,145 8	0,001 312 2	0,526 32	0,004 737	0,277 02	0,002 493	305,42	0,098 3	0,000 88
C_3H_8	0,978	44,096 2	43,126	0,200 1	0,195 698 0	0,584 90	0,572 032	0,342 11	0,334 584	369,82	0,153 2	0,149 83
n-C_4H_{10}	0,013	58,123 0	0,756	0,254 4	0,003 307 0	0,633 64	0,008 237	0,401 49	0,005 219	425,18	0,200 8	0,002 61
Σ			44,153		0,200 32		0,585 01		0,342 30			0,153 3

According to equation (20)

$$\begin{aligned} V^*_{\text{mix}} &= \frac{1}{4}\left[\sum x_i V_i^* + 3\left(\sum x_i V_i^{*2/3}\right)\left(\sum x_i V_i^{*1/3}\right)\right] \\ &= \frac{1}{4}(0{,}200\ 32 + 3 \times 0{,}342\ 30 \times 0{,}585\ 01) \\ &= 0{,}200\ 27 \end{aligned}$$

Combining equations (21) and (22) gives

$$\begin{aligned} T_{\text{c,mix}} &= \sum_{i=1}^{n} \sum_{j=1}^{n} x_i x_j V_i^{*1/2} T_{\text{c},i}^{1/2} V_j^{*1/2} T_{\text{c},j}^{1/2} / V^*_{\text{mix}} \\ &= [(0{,}009^2 \times 0{,}145\ 8 \times 305{,}42) + \\ &\quad + (0{,}009 \times 0{,}978 \times 0{,}145\ 8^{1/2} \times 305{,}42^{1/2} \times 0{,}200\ 1^{1/2} \times 369{,}82^{1/2}) + \\ &\quad + (0{,}009 \times 0{,}013 \times 0{,}145\ 8^{1/2} \times 305{,}42^{1/2} \times 0{,}254\ 4^{1/2} \times 425{,}18^{1/2}) + \\ &\quad + (0{,}978 \times 0{,}009 \times 0{,}200\ 1^{1/2} \times 369{,}82^{1/2} \times 0{,}145\ 8^{1/2} \times 305{,}42^{1/2}) + \\ &\quad + (0{,}978^2 \times 0{,}200\ 1 \times 369{,}82) \\ &\quad + (0{,}978 \times 0{,}013 \times 0{,}200\ 1^{1/2} \times 369{,}82^{1/2} \times 0{,}254\ 4^{1/2} \times 425{,}18^{1/2}) + \\ &\quad + (0{,}013 \times 0{,}009 \times 0{,}254\ 4^{1/2} \times 425{,}18^{1/2} \times 0{,}145\ 8^{1/2} \times 305{,}42^{1/2}) + \\ &\quad + (0{,}013 \times 0{,}978 \times 0{,}254\ 4^{1/2} \times 425{,}18^{1/2} \times 0{,}200\ 1^{1/2} \times 369{,}82^{1/2}) + \\ &\quad + (0{,}013^2 \times 0{,}254\ 4 \times 425{,}18)]/0{,}200\ 27 \end{aligned}$$

$$T_{\text{c,mix}} = 74{,}104\ 5/0{,}200\ 27 = 370{,}023$$

According to equation (17)

$$T_{\text{R}} = \frac{T}{T_{\text{c,mix}}}$$

where

$$T = t + 273{,}15 = -43 + 273{,}15 = 230{,}15\ \text{K}$$

Hence

$$T_{\text{R}} = \frac{230{,}15}{370{,}023} = 0{,}621\ 99$$

$$(1 - T_{\text{R}}) = 0{,}378\ 01$$

According to equation (15)

$$V_{R1} = 1 - 1{,}528\,16(1 - T_R)^{1/3} + 1{,}439\,07(1 - T_R)^{2/3} - 0{,}814\,46(1 - T_R) + 0{,}190\,454(1 - T_R)^{4/3}$$

$$= 1 - 1{,}528\,16 \times 0{,}378\,01^{1/3} + 1{,}439\,07 \times 0{,}378\,01^{2/3} - 0{,}814\,46 \times 0{,}378\,01 + 0{,}190\,454 \times 0{,}378\,01^{4/3}$$

$$V_{R1} = 0{,}391\,592$$

According to equation (16)

$$V_{R2} = (-0{,}296\,123 + 0{,}386\,194\,T_R - 0{,}042\,725\,8\,T_R^2 - 0{,}048\,064\,5\,T_R^3)/(T_R - 1{,}000\,1)$$

$$= \frac{(-0{,}296\,123 + 0{,}386\,194 \times 0{,}621\,99 - 0{,}042\,725\,8 \times 0{,}621\,99^2 - 0{,}048\,064\,5 \times 0{,}621\,99^3)}{(0{,}621\,99 - 1{,}000\,01)}$$

$$V_{R2} = 0{,}222\,24$$

Substituting V^*_{mix} for V^* in equation (13) gives

$$V_t = V^*_{\text{mix}} V_{R1}(1 - \omega_{\text{mix}} V_{R2})$$

$$= 0{,}200\,27 \times 0{,}391\,592(1 - 0{,}153\,3 \times 0{,}222\,24)$$

$$V_t = 0{,}075\,752$$

According to equation (14)

$$\varrho_t = \frac{\sum x_i M_i}{V_t}$$

$$\varrho_t = \frac{44{,}153}{0{,}075\,752} = 582{,}9\ \text{kg/m}^3$$

Annex H
(normative)

Critical temperature, acentric factor and characteristic volume of individual components used in equations

Table H.1

Component	Critical temperature $T_{c,i}$ K (see ref. [10])	Acentric factor ω_i (see ref. [9])	Characteristic volume V^* $m^3/kmol$ (see ref. [9])
CH_4	190,58	0,007 4	0,099 39
C_2H_6	305,42	0,098 3	0,145 8
C_3H_8	369,82	0,153 2	0,200 1
n-C_4H_{10}	425,18	0,200 8	0,254 4
i-C_4H_{10}	408,14	0,182 5	0,256 8
n-C_5H_{12}	469,65	0,252 2	0,311 3
i-C_5H_{12}	460,43	0,240 0	0,309 6
n-C_6H_{14}	507,43	0,300 7	0,368 2
n-C_7H_{16}	540,26	0,350 7	0,430 4
C_2H_4	282,36	0,088 2	0,131 0
C_3H_6	364,76	0,145 5	0,182 9
C_4H_8	419,57	0,192 1	0,237 7
N_2	126,2	0,035 8	0,090 12
O_2	154,58	0,029 8	0,073 82
CO_2	304,21	0,237 3	0,093 83
H_2S	373,54	0,103 9	0,099 41

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[9] Hankinson, R.W., and Thomson, G.H., COSTALD (Corresponding states liquid density) equation, *Hydrocarbon Processing*, Sept. 1979.

[10] *Engineering Data Book*, Gas Processors and Suppliers Association, 9th ed., 1972 (4th revision, 1979).

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Descriptors : petroleum products, natural gas, hydrocarbons, liquefied petroleum gases, liquefied natural gas, volume measurement, rules of calculation.

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