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Refrigerated hydrocarbon liquids — Static measurement — Calculation procedure

Hydrocarbures liquides réfrigérés — Mesurage statique — Procédure de calcul

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Contents

Page

Foreword ... **iv**

Introduction ... **v**

1 Scope ... **1**

2 Normative references ... **1**

3 Terms, definitions and symbols ... **1**
3.1 Terms and definitions ... 1
3.2 Symbols ... 2

4 Outline of calculation ... **3**
4.1 LPG ... 3
4.2 LNG ... 4
4.3 Data for calculation ... 4

5 Mass ... **5**
5.1 Mass of liquid phase ... 5
5.2 Correction for vapour phase ... 6
5.3 Mass in vacuum to mass in air ... 8

6 Energy content (calorific content) ... **8**

7 Inter-conversion of liquid mass and vapour volume at standard conditions ... **11**

8 Calculation of liquid density from composition ... **12**
8.1 General ... 12
8.2 LPG ... 12
8.3 LNG ... 13

9 Calculation of calorific value from composition ... **14**
9.1 Volumetric basis ... 14
9.2 Mass basis ... 14

Annex A (informative) **Characteristics of static measurement of refrigerated hydrocarbon liquids** ... **16**

Annex B (normative) **Molar volume of individual component** ... **17**

Annex C (normative) **Correction factors for volume reduction of LNG mixtures** ... **18**

Annex D (normative) **Gross calorific values for individual components** ... **19**

Annex E (normative) **Molar mass, compression factor and summation factor of individual component** ... **20**

Annex F (informative) **Boiling point of individual component** ... **21**

Annex G (informative) **Alternative procedure to calculate liquid density from composition** ... **22**

Bibliography ... **25**

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.

The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

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. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see www.iso.org/patents).

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For an explanation on the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT) see the following URL: www.iso.org/iso/foreword.html.

This document was prepared by Technical Committee ISO/TC 28, *Petroleum and related products, fuels and lubricants from natural or synthetic sources*, Subcommittee SC 5, *Measurement of refrigerated hydrocarbon and non-petroleum based liquefied gaseous fuels*.

This second edition cancels and replaces the first edition (ISO 6578:1991), which has been technically revised.

Introduction

Large quantities of refrigerated hydrocarbon liquids such as liquefied natural gas (LNG), liquefied petroleum gas (LPG), etc. are transported by marine carriers dedicated for these applications. These gases are traded based on static measurement on board marine carriers rather than the measurement at shore tanks or pipelines due mainly to the nature of the tank operation.

The measurement on board involves determination of liquid/vapour interface, i.e. liquid level, average temperatures of liquid and vapour, and vapour pressure in the tanks of marine carriers. The volumetric quantity of the liquid and gas is then computed with the tank capacity tables.

This document is applicable to calculate the volume at standard condition, liquid density from chemical composition, mass and energy content of fully refrigerated hydrocarbon liquids at a vapour pressure near to atmospheric pressure from the results of custody transfer measurement. This document is also applicable to ascertain the inventory in shore tanks. 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. No recommendations are given for the measurement of small parcels of refrigerated liquids, which are directly weighed.

Aspects of safety are not dealt with in this document. It is the responsibility of the user to ensure that the procedure of measurement meets applicable safety regulations.

Basic data and source references used in the calculation procedures are given in annexes.

Annexes A to G form an integral part of this document.

Refrigerated hydrocarbon liquids — Static measurement — Calculation procedure

1 Scope

This document specifies the calculation procedure to convert the volume of liquefied petroleum gas (LPG) and liquefied natural gas (LNG) under the conditions at the time of measurement to the equivalent volume of liquid or vapour at the standard condition, i.e. 15 °C and 101,325 kPaA, or to the equivalent mass or energy (calorific content). It applies to the quantities of refrigerated hydrocarbon liquids stored in or transferred to/from tanks and measured under static storage conditions. Calculation of pressurized gases is out of the scope of this document.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 91, *Petroleum and related products — Temperature and pressure volume correction factors (petroleum measurement tables) and standard reference conditions*

3 Terms, definitions and symbols

3.1 Terms and definitions

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

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

— ISO Online browsing platform: available at http://www.iso.org/obp

— IEC Electropedia: available at http://www.electropedia.org/

3.1.1
compression factor
actual (real) volume of a given amount of gas at a specified pressure and temperature divided by its volume, under the same conditions as calculated from the ideal gas law

[SOURCE: ISO 6976:2016, 3.10]

3.1.2
gross calorific value
amount of heat that would be released by the complete combustion with oxygen of a specified quantity of gas, in such a way that the pressure, p_1, at which the reaction takes place remains constant, and all the products of combustion are returned to the same specified temperature, t_1, as that of the reactants, all of these products being in the gaseous state except for water, which is condensed to the liquid state at t_1

Note 1 to entry: t_1 and p_1 are combustion reference temperature and combustion reference pressure, respectively.

[SOURCE: ISO 6976:2016, 3.1, modified — Note 1 to entry has been replaced.]

3.1.3
liquefied natural gas
LNG
liquid composed predominantly of methane

3.1.4
liquefied petroleum gas
LPG
liquid composed predominantly of any of the following hydrocarbons or mixtures thereof: propane, propene, butanes and butene

3.1.5
refrigerated hydrocarbon liquid
liquid composed predominantly of hydrocarbons, which are stored in a fully refrigerated condition at pressures near atmospheric

3.1.6
volumetric basis (ideal)
volume calculated on the basis that the vapour behaves like an ideal gas

3.1.7
volumetric basis (real)
volume calculated on the basis that the vapour behaves like a super-compressible gas

3.2 Symbols

The following symbols are defined here for use in this document, but additionally, some symbols are given more restricted meanings when used in some formulae. The restricted meaning is then given after the formulae.

$H_{s,m,i}$ gross (superior) calorific value on a mass basis, in megajoules per kilogram, of component i (see Table D.1)

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

$H_{s,V,i}$ gross (superior) calorific value on a volumetric basis (ideal), in megajoules per cubic metre, of component i (see Table D.1)

$H_{s,vol}$ gross (superior) calorific value on a volumetric basis, in megajoules per cubic metre, of the vapour at standard condition

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

m_{liq} mass, in kilograms, of liquid

M_i molar mass, in kilograms per kilomole, of component i (see Table E.1)

M_{mix} relative molar mass, in kilograms per kilomole, of the vapour mixture

P_s standard reference pressure, i.e. 101,325 kPaA (kilopascal absolute)

P_{vap} pressure, in kilopascals absolute, of the vapour in the container

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

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

R molar gas constant, 8,314 462 1 $J \cdot mol^{-1} \cdot K^{-1}$, see ISO 6976:2016, A.1

t temperature, in degrees Celsius, of the liquid

T_s standard reference temperature, i.e. 288,15 K (15 °C)

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

V_i molar volume, in cubic metres per kilomole, of component i, as a liquid at t

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

V_m ideal gaseous molar volume, in cubic metres per kilomole, at standard conditions:

i.e. $V_m = (R \times T_s)/P_s$ = 23,644 8 m^3/kmol at 15 °C and 101,325 kPaA (kilopascal absolute)

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

$V_{vap,s}$ vapour volume at standard condition

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

x_1 mole fraction of methane in the LNG

x_2 mole fraction of nitrogen in the LNG

Z_i compression factor for component i at the required pressure and temperature

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

ρ_s density, in kilograms per cubic metre, of the liquid at T_s

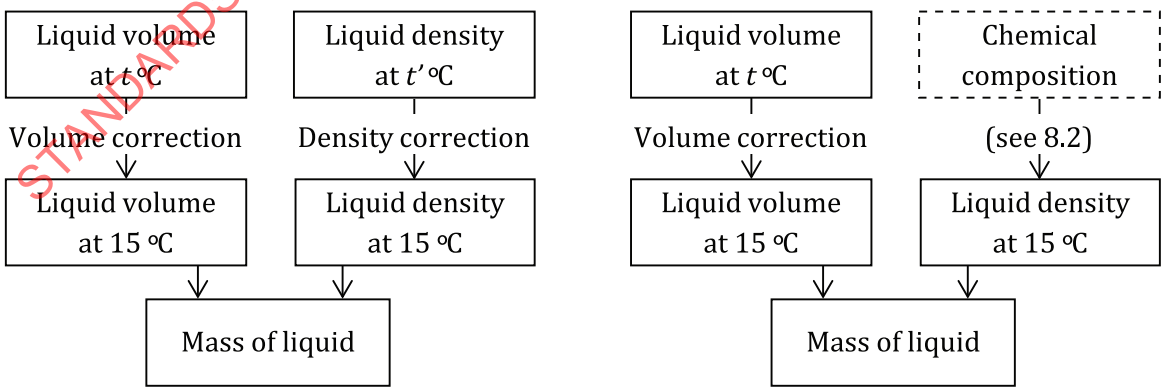
ρ_t density, in kilograms per cubic metre, of the liquid at t

NOTE 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.

4 Outline of calculation

4.1 LPG

Figure 1 outlines the calculation of mass of LPG from liquid volume at t °C.



a) Density by hydrometer **b) Density from composition**

Figure 1 — Calculation flow (LPG)

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 introduced in ISO 91 shall be used for volume corrections. Mass of LPG is calculated by multiplying its volume at standard temperature by its density at standard temperature.

b) The equivalent liquid content in the vapour space of a container holding refrigerated LPG is significantly less than the liquid in the container 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.

NOTE 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.

A condition in which a liquid has a vapour pressure significantly higher than atmospheric pressure at a standard temperature of 15 °C 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).

4.2 LNG

Figure 2 outlines the calculation energy content of LNG from liquid volume at t °C.

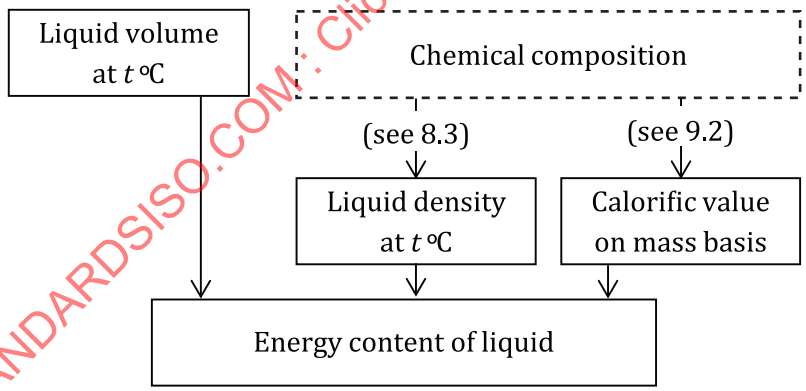


Figure 2 — Calculation flow (LNG)

Energy content of LNG is the product of its volume at observed temperature, the density at that temperature and the calorific value per unit mass. This calculation does not involve conversion of volume at observed temperature to the equivalent volume at standard temperature.

4.3 Data for calculation

Values specified in the normative annexes (Annexes B, C, D and E), such as physical properties of components of refrigerated hydrocarbon liquids, constants, factors, etc., shall be normatively applied in the use of this document.

5 Mass

5.1 Mass of liquid phase

5.1.1 The mass of liquid (m_{liq}), in kilograms, is calculated from Formula (1):

$$m_{liq} = V_{liq}\rho \tag{1}$$

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

EXAMPLE 1

Measured volume of liquid LNG in a container = 45 550 m^3 at −159,5 °C.

Calculated density at −159,5 °C = 462,4 kg/m^3

Mass of LNG (m_{liq}) = 45 550 × 462,4 = 21,06 × 10^6 kg or 21,06 × 10^3 *t*

5.1.2 The density of refrigerated LPG may be determined at the standard temperature of 15 °C by use of the pressure hydrometer method (see ISO 3993) or suitable densimeter. 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.

The density of liquid may also 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 using Formula (2). The density at t_1 shall be measured or calculated if the difference of the temperatures exceeds 5 °C.

$$\rho_{t,1} = \rho_{t,2} + F\left(t_2 - t_1\right) \tag{2}$$

where

$\rho_{t,1}$ and $\rho_{t,2}$ 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 $kg/(m^3 \cdot °C)$.

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

EXAMPLE 2

The density of the LNG is 463,1 kg/m^3 at t_2 = –160,0 °C.

What is the density of the LNG at - 159,5 °C?

Substituting into Formula (2) gives:

$\rho_{t,1}$ = 463,1 + 1,4[–160,0 – (–159,5)]

= 463,1 – 0,7

= 462,4 kg/m^3

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 equilibrium conditions, Formula (3) can be applied to measurements made in either the delivery or the receiving container.

Mass transferred = |Final mass – Initial mass|

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

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

If it is impractical to measure the density of the liquid in a container, ρ_F and ρ_I cannot be determined. By using the measured density of the liquid being transferred, however, the simplified Formulae (3a) and (3b) may be employed to calculate the mass of product transferred.

At delivery container: $$m = V_{\mathrm{liq}}\rho - \left(V_{\mathrm{liq}} \times \frac{T_\mathrm{s}}{T_{\mathrm{vap},F}} \times \frac{P_{\mathrm{vap},F}}{P_\mathrm{s}} \times \frac{M_{\mathrm{mix},F}}{V_\mathrm{m} Z_{\mathrm{mix},F}} \right) \quad (3a)$$

At receiving container: $$m = V_{\mathrm{liq}}\rho - \left(V_{\mathrm{liq}} \times \frac{T_\mathrm{s}}{T_{\mathrm{vap},I}} \times \frac{P_{\mathrm{vap},I}}{P_\mathrm{s}} \times \frac{M_{\mathrm{mix},I}}{V_\mathrm{m} Z_{\mathrm{mix},I}} \right) \quad (3b)$$

where

$V_{\mathrm{liq}} = |V_{\mathrm{liq},F} - V_{\mathrm{liq},I}|$;

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

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

$$m = V_{\mathrm{liq},F}\,\rho + \left(V_{\mathrm{vap},F} \times \frac{T_{\mathrm{s}}}{T_{\mathrm{vap}}} \times \frac{P_{\mathrm{vap}}}{P_{\mathrm{s}}} \times \frac{M_{\mathrm{mix}}}{V_{\mathrm{m}} Z_{\mathrm{mix}}} \right) \tag{3c}$$

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 Formula (3a) or (3b) may be used in practice.

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 compression 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 molar mass and compression factor of the vapour mixture (M_{mix}, Z_{mix}).

NOTE For measurements in a receiving container, Formula (3b) 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

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

Volume of liquid LNG transferred at temperature t = 45 550 m^3

Measured temperature of liquid, t = –159,5 °C

Liquid density at –159,5 °C = 462,4 kg/m^3

Average temperature of vapour after transfer = –118 °C = 155,15 K

Pressure of vapour after transfer = 110,0 kPaA

It may be assumed that the molar mass of the vapour mixture is that of pure methane (see Table E.1). = 16,042 kg/kmol

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

$$m = \left[(45\,550 \times 462{,}4) - \left(45\,550 \times \frac{288{,}15}{155{,}15} \times \frac{110{,}0}{101{,}325} \times \frac{16{,}042}{23{,}644\,8} \right) \right]$$

$$= 21\,062\,320 - 62\,309$$

$$= 21\,000 \times 10^3\ \mathrm{kg}$$

or 21 000 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)	233,15	250,15
Pressure in container vapour space (kPaA)	108,0	112,0

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

Substituting into Formula (3) gives:

$$m = \left[(45\,550\times 507)+\left(950\times\frac{288,15}{233,15}\times\frac{108,0}{101,325}\times\frac{44,153}{23,644\,8}\right)\right]-$$
$$\left[(850\times 507)+\left(40\,000\times\frac{288,15}{250,15}\times\frac{112,0}{101,325}\times\frac{44,153}{23,644\,8}\right)\right]$$
$$=(23\,093\,850+2\,337)-(430\,950+95\,105)$$
$$=22\,570\times 10^3\ \text{kg}$$
$$\text{or } 22\,570\,t$$

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.

5.3 Mass in vacuum to mass in air

The current practice for measurement of LPG is by apparent mass in air. The tables for kilogram per cubic metre at 15 °C and cubic metres at 15 °C per metric ton against density at 15 °C introduced in ISO 91 may be used to convert mass into apparent mass in air.

6 Energy content (calorific content)

6.1 The energy content of the liquid is calculated by using Formula (4):

$$Q_{liq} = m_{liq} H_{s,m} \tag{4}$$

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, Formula (5) applies to measurements made in either the delivery or the receiving container.

Energy transferred = |Final energy content − Initial energy content|

$$\therefore Q = \left| \left[V_{liq,F}\,\rho_F H_{s,m,F} + V_{vap,F}\times\frac{T_s}{T_{vap,F}}\times\frac{P_{vap,F}}{P_s}\times H_{s,vol,F} \right] - \left[V_{liq,I}\,\rho_I H_{s,m,I} + V_{vap,I}\times\frac{T_s}{T_{vap,I}}\times\frac{P_{vap,I}}{P_s}\times H_{s,vol,I} \right] \right| \tag{5}$$

where

$H_{s,vol} = \frac{M_{mix}}{V_m Z_{mix}} \times H_{s,m}$ = the gross calorific value on volumetric basis, in megajoules per cubic metre, of the vapour at standard condition.

If it is impractical to measure the density of the liquid in a container, ρ_F and ρ_I cannot be determined. By using the measured density of the liquid being transferred, however, the simplified Formulae (5a) and (5b) may be employed to calculate the net energy transferred.

At delivery container: $$Q = V_{liq}\rho H_{s,m} - V_{liq} \times \frac{T_s}{T_{vap,F}} \times \frac{P_{vap,F}}{P_s} \times H_{s,vol} \quad (5a)$$

At receiving container: $$Q = V_{liq}\rho H_{s,m} - V_{liq} \times \frac{T_s}{T_{vap,I}} \times \frac{P_{vap,I}}{P_s} \times H_{s,vol} \quad (5b)$$

where

$V_{liq} = |V_{liq,F} - V_{liq,I}|$;

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

$H_{s,vol}$ is the estimated gross calorific value of the transferred gas at standard condition.

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

$$Q = V_{liq}\rho H_{s,m} + V_{vap} \times \frac{T_s}{T_{vap}} \times \frac{P_{vap}}{P_s} \times H_{s,vol} \quad (5c)$$

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 Formula (5a) or (5b) may be used in practice.

NOTE For measurements in a receiving container, Formula (5b) 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

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

Volume of liquid LNG transferred at temperature t	= 45 550 m^3
Liquid temperature, t	= –159,5 °C
Liquid density at –159,5 °C	= 462,4 kg/m^3
Average temperature of vapour after transfer	= –118 °C = 155,15 K
Pressure of vapour after transfer	= 110,0 kPaA
Gross calorific value on mass basis of the liquid using EXAMPLE 1 given in 9.2, i.e. $H_{s,m}$	= 54,224 MJ/kg
It may be assumed that the gross calorific value on volumetric basis for the vapour mixture is that for pure methane at standard condition (see Table D.1).	= 37,704 MJ/m^3

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

$$Q = 45\,550 \times 462,4 \times 54,224 - 45\,550 \times \frac{288,15}{155,15} \times \frac{110,0}{101,325} \times 37,704$$

$$= 1\,142,083 \times 10^6 - 3,463 \times 10^6$$

$$= 1\,138,6 \times 10^6 \text{ MJ}$$

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 (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)	233,15	250,15
Pressure in container vapour space (kPaA)	108,0	112,0

Gross calorific value on mass basis for the liquid, using EXAMPLE 2 given in 9.2, i.e. $H_{s,m}$ = 50,360 MJ/kg.

It may be assumed that the gross calorific value on volumetric basis for the vapour mixture is that for pure propane at 101,325 kPaA and 15 °C (see Table D.1), i.e. $H_{s,vol}$ = 93,94 MJ/m^3.

Substituting into Formula (5) gives:

$$Q = \left[(45\,550 \times 507 \times 50,360) + \left(950 \times \frac{288,15}{233,15} \times \frac{108,0}{101,325} \times 93,94 \right) \right]$$

$$- \left[(850 \times 507 \times 50,360) + \left(40\,000 \times \frac{288,15}{250,15} \times \frac{112,0}{101,325} \times 93,94 \right) \right]$$

$$= \left(1\,163,01 \times 10^6 + 0,12 \times 10^6 \right) - \left(21,70 \times 10^6 + 4,78 \times 10^6 \right)$$

$$= 1\,136,7 \times 10^6 \text{ MJ}$$

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 Formula (6a)

$$V_{\text{vap,s}} = \frac{m_{\text{liq}} V_{\text{m}} Z_{\text{mix}}}{M_{\text{mix}}} \tag{6a}$$

or Formula (6b)

$$m_{\text{liq}} = \frac{V_{\text{vap,s}} M_{\text{mix}}}{V_{\text{m}} Z_{\text{mix}}} \tag{6b}$$

where

$V_{\text{vap,s}}$ is vapour volume at the standard conditions;

$M_{\text{mix}} = \Sigma x_i M_i$.

7.2 The compression factor which is commonly used to calculate the volume of a vapour mixture at standard conditions is given by Formula (7):

$$Z_{\text{mix}} = 1 - [\Sigma x_i (1 - Z_i)^{1/2}]^2 \tag{7}$$

Values of the molar mass M_i and summation factor $(1 - Z_i)^{1/2}$ for the various components are given in Table E.1.

EXAMPLE 1

Calculate the compression factor at standard condition 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_{10}	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 1 — Compression factor at standard condition

Component	M_i	x_i	$x_i M_i$	$(1 - Z_i)^{1/2}$	$x_i (1 - Z_i)^{1/2}$
CH_4	16,042	0,900	14,437 8	0,044 5	0,040 1
C_2H_6	30,069	0,049	1,473 4	0,091 9	0,004 5
C_3H_8	44,096	0,029	1,278 8	0,134 4	0,003 9
n-C_4H_{10}	58,122	0,013	0,755 6	0,184 0	0,002 4
i-C_4H_{10}	58,122	0,004	0,232 5	0,172 2	0,000 7
n-C_5H_{12}	72,149	0,001	0,072 1	0,236 1	0,000 2
N_2	28,013	0,004	0,112 1	0,017 0	0,000 1
Σ	—	1,000	18,362 3	—	0,051 9

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

$= 1 - (0{,}051\ 9)^2$

$= 0{,}997\ 3$

EXAMPLE 2

Calculate the equivalent volume of vapour at standard conditions corresponding to a mass of 21 062 *t* of LNG.

Assume the molar mass $M_{mix} = 18{,}362\ 3$

Assume the compression factor $Z_{mix} = 0{,}997\ 3$

$V_m = 23{,}644\ 8\ m^3/kmol$ at 15 °C, 101,325 kPaA (see 3.2)

$$V_{vap,s} = 21{,}062 \times 10^3 \times 23{,}644\ 8 \times \frac{0{,}997\ 3}{18{,}362\ 3}$$

$= 27{,}048 \times 10^3\ m^3$ at 101,325 kPaA, 15 °C

8 Calculation of liquid density from composition

8.1 General

Given molar fraction of each component, the density of refrigerated hydrocarbon liquids can be calculated by dividing the average molar mass by the average saturated molar volume. To achieve accurate density of a refrigerated hydrocarbon liquid that consists of more than two components, reduction in volume on mixing components should be allowed.

8.2 LPG

The density at reference temperature of LPG having propane or butane as its main constituent can be calculated from Formula (8), which does not make allowance for the reduction in volume on mixing components:

$$\rho_s = \frac{\Sigma(x_i M_i)}{\Sigma(x_i V_i)} \tag{8}$$

where

V_i is the molar volumes of each component (see Table B.1 for molar volumes at 15 °C).

NOTE See Annex G for alternative calculation procedures.

EXAMPLE

Calculate the density at 15 °C of LPG having the following molar composition (see Table 2).

Table 2 — Density at 15 °C of LPG

Component	M_i	x_i	x_iM_i	V_i at 15 °C	x_iV_i
C_2H_6	30,069	0,009	0,271	0,083 99	0,000 756
C_3H_8	44,096	0,978	43,126	0,086 87	0,084 959
n-C_4H_{10}	58,122	0,013	0,756	0,099 41	0,001 292
Σ	—	1,000	44,153	—	0,087 007

$$\rho_s = \frac{44,153}{0,087\,007}$$

$$= 507,5 \text{ kg/m}^3$$

8.3 LNG

For LNG mixture having an average molar 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, at temperatures between –167,15 °C and –155,15 °C, the reduction in volume on mixing components is given by the revised Klosek-McKinley equation:

$$\rho_t = \frac{\Sigma(x_i M_i)}{\Sigma(x_i V_i) - V_c} \tag{9}$$

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

where

V_i is the molar volume of each component at t as given in Table B.2;

V_c is the reduction in volume on mixing components;

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

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

EXAMPLE

Calculate the density at –159,5 °C of LNG having the same composition as EXAMPLE 1 in 7.2.

Table 3 — Density at -159,5 °C of LNG

Component	M_i	x_i	x_iM_i	V_i at –159,5 °C	x_iV_i
CH_4	16,042	0,900	14,437 8	0,038 215	0,034 394
C_2H_6	30,069	0,049	1,473 4	0,047 984	0,002 351
C_3H_8	44,096	0,029	1,278 8	0,062 542	0,001 814
n-C_4H_{10}	58,122	0,013	0,755 6	0,076 923	0,001 000
i-C_4H_{10}	58,122	0,004	0,232 5	0,078 403	0,000 314
n-C_5H_{12}	72,149	0,001	0,072 1	0,091 636	0,000 092
N_2	28,013	0,004	0,112 1	0,047 362	0,000 189
Σ	—	1,000	18,362 3	—	0,040 154

Average molar mass = 18,362 3

Factor $k_1 = 0,483 \times 10^{-3}$ obtained by interpolation in Table C.1.

Factor $k_2 = 0{,}763 \times 10^{-3}$ obtained by interpolation in Table C.2.

$$V_c = \left[0{,}000\,483 + (0{,}000\,763 - 0{,}000\,483) \times \frac{0{,}004}{0{,}042\,5}\right] \times 0{,}900$$

$$= 0{,}000\,458$$

$$\rho_t = \frac{18{,}362\,3}{(0{,}040\,154 - 0{,}000\,458)}$$

$$= 462{,}6\ \text{kg/m}^3$$

9 Calculation of calorific value from composition

9.1 Volumetric basis

The gross calorific value, on a volumetric basis, of a mixture may be calculated from Formula (11):

$$H_{s,vol} = \frac{\Sigma x_i H_{s,V,i}}{Z_{mix}} \tag{11}$$

where

$H_{s,V,i}$ is the gross calorific value on a volumetric basis (ideal) of component i given in Table D.1.

EXAMPLE

Calculate the gross heating value on a volumetric basis of LNG having the same composition as EXAMPLE 1 in 7.2.

Table 4 — Gross heating value on a volumetric basis of LNG

Component	x_i	$H_{s,V,i}$ at 101,325 kPaA, 15 °C MJ/m³	$x_i H_{s,V,i}$
CH_4	0,900	37,704	33,934
C_2H_6	0,049	66,07	3,237
C_3H_8	0,029	93,94	2,724
n-C_4H_{10}	0,013	121,79	1,583
i-C_4H_{10}	0,004	121,40	0,486
n-C_5H_{12}	0,001	149,66	0,150
N_2	0,004	0	0,000
Σ	1,000	—	42,114

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

$$H_{s,vol} = \frac{42{,}114}{0{,}997\,3}$$

$$= 42{,}23\ \text{MJ/m}^3$$

9.2 Mass basis

The gross calorific value, on a mass basis, of a mixture may be calculated from Formula (12):

$$H_{s,m} = \Sigma H_{s,m,i} \left[\frac{x_i M_i}{\Sigma(x_i M_i)}\right] \tag{12}$$

where

$H_{s,m,i}$ is the gross calorific value on a mass basis of component *i* given in Table D.1.

EXAMPLE 1

Calculate the gross heating value on a mass basis of LNG having the same composition as EXAMPLE 1 in 7.2.

Table 5 — Gross heating value on a mass basis of LNG

Component	M_i	x_i	$x_i M_i$	$\frac{x_i M_i}{\Sigma(x_i M_i)}$	$H_{s,m,i}$ 15 °C MJ/kg	$H_{s,m,i} \times \frac{x_i M_i}{\Sigma(x_i M_i)}$
CH_4	16,042	0,900	14,437 8	0,786 3	55,573	43,697
C_2H_6	30,069	0,049	1,473 4	0,080 2	51,952	4,167
C_3H_8	44,096	0,029	1,278 8	0,069 6	50,370	3,506
n-C_4H_{10}	58,122	0,013	0,755 6	0,041 1	49,547	2,036
i-C_4H_{10}	58,122	0,004	0,232 5	0,012 7	49,389	0,627
n-C_5H_{12}	72,149	0,001	0,072 1	0,003 9	49,046	0,191
N_2	28,013	0,004	0,112 1	0,006 1	0	0
Σ	—	1,000	18,362 3	—	—	54,224

Gross calorific value on mass basis of the mixture $H_{s,m}$ = 54,224 MJ/kg.

EXAMPLE 2

Calculate the gross heating value on a mass basis of LPG having the same composition as the EXAMPLE in 8.2.

Table 6 — Gross heating value on a mass basis of LPG

Component	M_i	x_i	$x_i M_i$	$\frac{x_i M_i}{\Sigma(x_i M_i)}$	$H_{s,m,i}$ 15 °C MJ/kg	$H_{s,m,i} \times \frac{x_i M_i}{\Sigma(x_i M_i)}$
C_2H_6	30,069	0,009	0,271	0,006 1	51,952	0,317
C_3H_8	44,096	0,978	43,126	0,976 7	50,370	49,196
n-C_4H_{10}	58,122	0,013	0,756	0,017 1	49,547	0,847
Σ	—	1,000	44,153	—	—	50,360

Gross calorific value on mass basis of the mixture $H_{s,m}$ = 50,360 MJ/kg.

Annex A
(informative)

Characteristics of static measurement of refrigerated hydrocarbon liquids

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 reliquefaction.

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) should 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 emphasized 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.

Annex B
(normative)

Molar volume of individual component

Table B.1 — Molar volume of individual component in LPG

Component	Molar volume V_i, m^3/kmol at 15 °C
C_2H_6	0,083 99
C_3H_8	0,086 87
n-C_4H_{10}	0,099 41
i-C_4H_{10}	0,103 18
n-C_5H_{12}	0,114 37
i-C_5H_{12}	0,115 51
C_3H_6	0,080 52
n-C_4H_8	0,093 30
Source: JIS K 2240:2013, Table 16.	

Table B.2 — Orthobaric molar volume of individual component in LNG

Component	Molar volume V_i, m^3/kmol						
	118 K	116 K	114 K	112 K	110 K	108 K	106 K
	−155,15 °C	−157,15 °C	−159,15 °C	−161,15 °C	−163,15 °C	−165,15 °C	−167,15 °C
CH_4	0,038 817	0,038 536	0,038 262	0,037 995	0,037 735	0,037 481	0,037 234
C_2H_6	0,048 356	0,048 184	0,048 014	0,047 845	0,047 678	0,047 512	0,047 348
C_3H_8	0,062 939	0,062 756	0,062 574	0,062 392	0,062 212	0,062 033	0,061 855
n-C_4H_{10}	0,077 344	0,077 150	0,076 957	0,076 765	0,076 574	0,076 384	0,076 194
i-C_4H_{10}	0,078 844	0,078 640	0,078 438	0,078 236	0,078 035	0,077 836	0,077 637
n-C_5H_{12}	0,092 095	0,091 884	0,091 673	0,091 462	0,091 252	0,091 042	0,090 833
i-C_5H_{12}	0,092 251	0,092 032	0,091 814	0,091 596	0,091 379	0,091 163	0,090 948
N_2	0,050 885	0,049 179	0,047 602	0,046 231	0,045 031	0,043 963	0,043 002
NOTE The exact correction factor at given liquid temperature and molar mass is obtained by interpolation, assuming exact linearity between adjacent values in the table.							
Source: Reference [11].							

Annex C
(normative)

Correction factors for volume reduction of LNG mixtures

Table C.1 — Correction factor k_1

Molar mass of mixture $\Sigma x_i M_i$	$k_1 \times 10^3$ m³/kmol			
	120 K	115 K	110 K	105 K
	−153,15 °C	−158,15 °C	−163,15 °C	−168,15 °C
16	−0,01	−0,009	−0,008	−0,007
17	0,250	0,220	0,180	0,165
18	0,500	0,440	0,375	0,340
19	0,695	0,610	0,535	0,475
20	0,920	0,810	0,725	0,635

NOTE The exact correction factor at given liquid temperature and molar mass is obtained by interpolation, assuming exact linearity between adjacent values in the table.

The above values of correction factor k_1 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 in 8.3).

Source: Reference [11].

Table C.2 — Correction factor k_2

Molar mass of mixture $\Sigma x_i M_i$	$k_2 \times 10^3$ m³/kmol			
	120 K	115 K	110 K	105 K
	−153,15 °C	−158,15 °C	−163,15 °C	−168,15 °C
16	−0,032	−0,024	−0,015	−0,01
17	0,60	0,41	0,32	0,24
18	0,91	0,72	0,59	0,42
19	1,23	0,95	0,77	0,61
20	1,43	1,15	0,92	0,75

NOTE The exact correction factor at given liquid temperature and molar mass is obtained by interpolation, assuming exact linearity between adjacent values in the table.

The above values of correction factor 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 in 8.3).

Source: Reference [11].

Annex D
(normative)

Gross calorific values for individual components

Table D.1 — Gross calorific values for individual components

Component	Gross calorific value on mass basis[a] $H_{s,m,i}$ (MJ/kg)	Gross calorific value on volumetric basis (ideal)[b] $H_{s,V,i}$ (MJ/m^3)
CH_4	55,573	37,704
C_2H_6	51,952	66,07
C_3H_8	50,370	93,94
n-C_4H_{10}	49,547	121,79
i-C_4H_{10}	49,389	121,40
n-C_5H_{12}	49,046	149,66
i-C_5H_{12}	48,950	149,36
n-C_6H_{14}	48,718	177,55
n-C_7H_{16}	48,474	205,42
C_2H_4	50,338	59,72
C_3H_6	48,941	87,10
C_4H_8 (mean)	48,306	114,62
H_2S	16,501	23,78

[a] Derived from ISO 6976:2016, Table 1 and Table 3; combustion reference temperature is 15 °C.

[b] Derived from ISO 6976:2016, Table 3; combustion reference temperature and metering reference temperature are 15 °C; combustion reference pressure and metering reference pressure are 101,325 kPaA.