International Standard 6146

INTERNATIONAL ORGANIZATION FOR STANDARDIZATION•МЕЖДУНАРОДНАЯ ОРГАНИЗАЦИЯ ПО СТАНДАРТИЗАЦИИ•ORGANISATION INTERNATIONALE DE NORMALISATION

Gas analysis — Preparation of calibration gas mixtures — Manometric method

Analyse des gaz — Préparation des mélanges de gaz pour étalonnage — Méthode par voie manométrique

First edition — 1979-05-01

UDC 543.27 : 53.089.68 **Ref. No. ISO 6146-1979 (E)**

Descriptors : gases, gas mixtures, chemical analysis, gas analysis, test specimen conditioning, manometric methods.

Price based on 19 pages

FOREWORD

ISO (the International Organization for Standardization) is a worldwide federation of national standards institutes (ISO member bodies). The work of developing International Standards is carried out through ISO technical committees. Every member body interested in a subject for which a technical committee has been set up 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.

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

International Standard ISO 6146 was developed by Technical Committee ISO/TC 158, *Analysis of gases*, and was circulated to the member bodies in November 1977.

It has been approved by the member bodies of the following countries :

Australia
Belgium
Czechoslovakia
Egypt, Arab Rep. of
France
Germany, F. R.
India
Ireland
Mexico
Netherlands
Philippines
Poland
Romania
South Africa, Rep. of
Spain
Turkey
USA
USSR
Yugoslavia

The member body of the following country expressed disapproval of the document on technical grounds :

United Kingdom

Printed in Switzerland

Gas analysis — Preparation of calibration gas mixtures — Manometric method

1 SCOPE AND FIELD OF APPLICATION

This International Standard specifies a manometric method for the preparation of calibration gas mixtures for which the accuracy of the concentration of each component may vary within very wide limits, depending on the mixtures being prepared. For example, a relative accuracy of 1 %, on a concentration expressed in pressure ratio or mole fraction[1], may be obtained in the case of mixtures of gases which approach ideal gases[2], but with certain gases, such as hydrocarbons or polar compounds for example, the potential errors may be very much greater.

Considering the fact that the methods of calculation employed (Dalton, Amagat or Kay) are not absolutely rigorous, this manometric method is often used to obtain a first approximation of the desired concentrations, and these concentrations are subsequently measured by a comparison method and, if need be, by a direct analytical method.

2 REFERENCE

ISO 6141, *Gas analysis — Calibration gas mixtures — Certificate of mixture preparation.*

3 PRINCIPLE

The method is a static method which permits the preparation of large volumes of calibration gas mixtures which are available under pressure.

The components A, B, C, etc. and the make-up gas are injected successively into an enclosure presumed to be of constant volume, which has previously been cleaned and evacuated (the expansion of the enclosure due to variations of its internal pressure is neglected).

After each injection, the pressure in the enclosure is measured.

The concentration of the calibration gas is equal to the ratio of the pressure change caused by the introduction of the calibration component to the total pressure of the gas mixture, and is expressed in terms of a pressure ratio.

The conversion of a concentration expressed in terms of a pressure ratio into a concentration expressed in terms of a mole fraction is obtained by different methods of calculation, the most common of which are :

- Dalton's method;
- Amagat's method;
- Kay's method.

These methods are described in annex B.

4 PRACTICAL EXAMPLE

4.1 Description of the filling system

The manometric filling system is illustrated schematically in figure 1.

The previously cleaned cylinders to be filled (3) are connected to a manifold (1) comprising a series of pressure gauges (5 to 10) which cover the range of pressures involved. At least one of these pressure gauges shall be a vacuum gauge (5) capable of measuring the pressure in the evacuated manifold cylinders for the calibration gas, prior to the admission of the calibration components.

The pressure gauges shall have a relative accuracy adapted to the accuracy desired. For example, for a relative accuracy of 1 % with respect to the concentration, the pressure gauges shall have a relative accuracy of at least 0,5 %.

The cylinders with the gases to be mixed (calibration components) (13) are likewise connected to a manifold (2). The two manifolds (1) and (2) are connected via a valve (16).

Volatile components may be injected from liquefied gases, cooled to limit their partial pressure, by means of the device (14-15).

The cylinders and all the components of the filling system shall be designed for the maximum pressure which may arise, or shall be protected in an appropriate manner. This condition applies particularly to the pressure gauges and to the vacuum systems.

---

[1] The transformation of the value of concentration from one set of units to another becomes more difficult as one gaseous component nears its saturation point.

[2] Annex A gives a brief review of the properties of ideal and non-ideal gases.

4.2 Operating procedure

The gases shall be introduced into the device by observing the following procedure :

The manifolds and the cylinders to be filled are evacuated together down to a pressure compatible with the desired mixture and it is checked that this residual pressure is stable after the pumping system has been isolated; the first component is then introduced into the empty cylinders. When the desired pressure is reached, the reading is noted, but the pressure must be allowed to rise slowly so as to avoid errors caused by large changes in temperature. After that, all the valves are closed and the manifold is again evacuated. The second component is then introduced into the manifold at a pressure slightly higher than that of the first component, in order to prevent the escape of the latter. It is then introduced into the gas cylinders under the desired pressure. The other components are introduced by repeating the same procedure until all have been injected. Concentrations of the order of 10^{-6} expressed in terms of pressure ratio can be prepared by evacuating the device and then injecting the component. The latter, present in trace amounts, is then conveyed into the calibration gas cylinder which will be filled with the appropriate make-up gas.

Assuming an ideal behaviour of the component according to Dalton's law, which states that the total pressure of a mixture is equal to the sum of the partial pressures of the components of this mixture, i.e.

$$p = \sum_{i=1}^{n} p_i$$

the molar concentration is calculated as follows :

$$x_i = \frac{p_i}{p}$$

If the behaviour of real gases rather than that of ideal gases is considered, it becomes necessary to correct the values of p_i accordingly.[1]

As each component is introduced into the mixture, any increase in temperature must be taken into consideration. It is, therefore, necessary either to make an appropriate correction calculation or to wait until the entire apparatus has regained its initial ambient temperature before taking a pressure reading and introducing the next component.

It is generally preferable to introduce first the gas whose Z-coefficient[2] deviates farthest from unity, provided that it is not the principal component of the mixture. The reason for this is that if this gas is introduced last, it is in the most compressed form and, as a result, introduces the largest error.

Since the mutual diffusion of the components is generally not rapid enough to homogenize the mixture during the filling process, a piston effect on one component is evident when the next component is introduced. When the homogenization has ultimately taken place, the mixture has, in general, a lower Z-coefficient and, since the total mass remains unchanged, there is generally an increase in the pressure. It has been found experimentally that the variation may amount to a few percent. This leads to a sizeable error which can be minimized by adjusting the final theoretical pressure only after waiting – after a first charge at a purposely lower pressure – until no further change takes place.

The time required for the homogenization must also be taken into consideration. It is a function of the dimensions and geometry of the container, of the turbulence caused during injection, and of the mutual diffusion coefficients of the gases. Natural homogenization of gas mixtures may require a delay of several weeks; it is possible to accelerate the process, by mechanical agitation for example.

Products which are normally liquid at ambient temperature may also be used to fill the cylinders since they have a certain vapour pressure which is a function of their nature and of their volatility. The vapour pressure of these liquids must, however, be higher than their partial pressure in the gaseous mixture at the lowest temperature at which the sample is being used. In other words, if the pressure becomes too high (or if the temperature becomes too low), there will be some condensation of the vapour, and the concentration of the component in the mixture will not be constant.

A common rule is to take

$$p_i \leqslant 0{,}7\, p_{Si}$$

where p_i is the partial pressure of the component i and p_{Si} is the liquefaction pressure at the minimum conservation temperature (see the certificate of mixture preparation described in ISO 6141).

5 ACCURACY

The accuracy of the concentration of a mixture prepared in this manner depends on several factors and particularly on the nature of the gases. Under the most favourable conditions, i.e. under perfectly isothermal conditions and at pressures which, for the gas in question, correspond to Z-coefficients approximately equal to 1, the accuracy is approximately that of the pressure measurements :

$$\text{if} \quad \frac{\Delta p_1}{p_1} = \frac{\Delta p_2}{p_2} < 10^{-2}$$

$$\text{then} \quad \frac{\Delta x_1}{x_1} < 2 \times 10^{-2}$$

This is the case with mixtures of gases (called "permanent") comprising nitrogen, oxygen, hydrogen, helium, argon and neon, as long as their partial pressures do not exceed about 10 bar.

---

1) See annexes A and B.

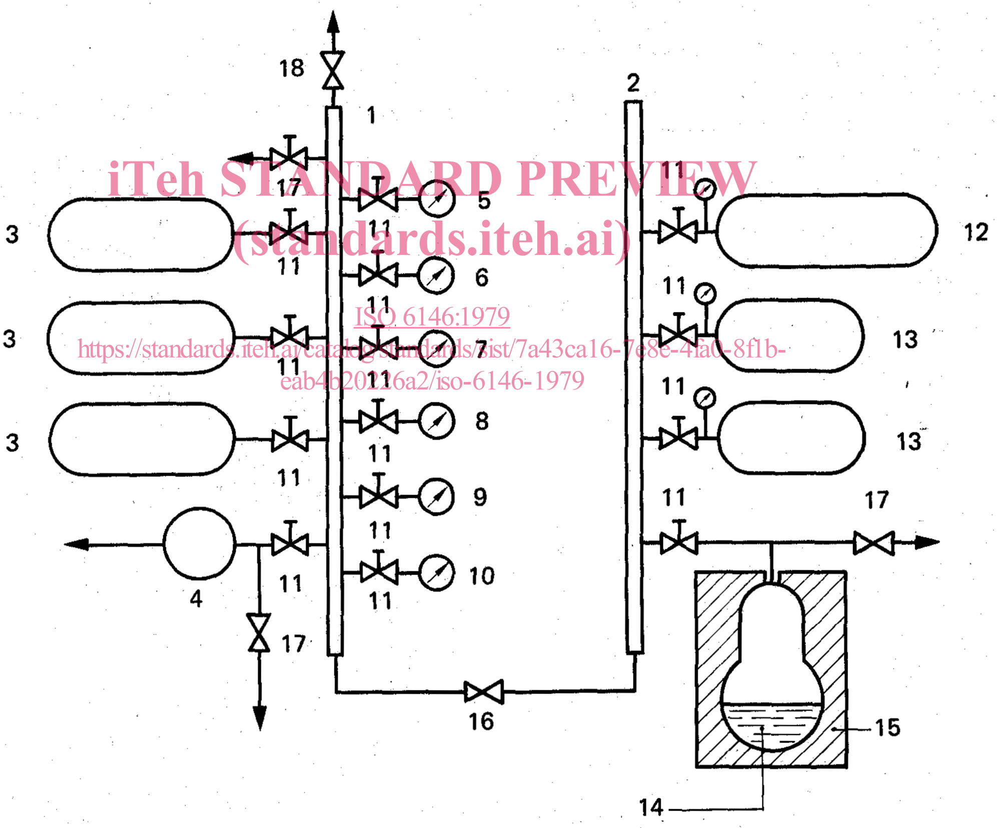
2) See A.4 and A.5.

On the other hand, with a $CO_2 + H_2$ mixture, deviation in the relative value of as much as 20 % may occur. Annex C gives examples of calculations showing the various deviations which may be found.

There are a certain number of restrictions which must be known before this method is employed. Large deviations from the specified concentrations may occur if one or more components become liquefied or if the values of the Z-coefficient are not applicable under the operating conditions. A deviation from the expected values may also occur if the heat liberated by the compression is neglected or if it is impossible to dissipate this heat between the addition of successive components. Important errors in the mixture composition may also be found if the mixtures react. Certain mixtures can indeed react — even at concentrations of the order of 10^{-6} expressed in terms of pressure ratio — examples being oxygen and hydrogen, chlorine and hydrogen, nitrogen monoxide and dioxide and unsaturated hydrocarbons in the presence of sulphur compounds. Errors also occur as a result of the normal consequences of the polymerization of certain compounds (0,5 % hydrogen cyanide, for example) or decomposition [for example of $Ni(CO)_4$] unless suitable stabilizers are added.

6 PRECAUTIONS TO BE TAKEN

The principal hazard in using manometric methods is the danger resulting from the manipulation of pressurized devices containing mixtures which are reactive or could pass through an explosive zone during preparation. For example, the compression of pure oxygen in the presence of hydrocarbons is dangerous, since, during the cylinder filling, the composition of the mixture varies and may go through the explosive zone; certain gases, even when pure, such as acetylene, explode upon compression.



1	Proportioning manifold
2	Filling manifold
3	Calibration gas cylinders
4	Vacuum pump
5 to 10	Manometers
11	Stopcocks
12	Make-up gas cylinder
13	Cylinders containing calibration constituents
14	Cylinder for readily volatile liquefied gas
15	Cooling device, if necessary
16	Regulating and cut-off valve
17	Safety valve
18	Purging and relief valve

FIGURE 1 — **Diagram of manometric filling system for preparation of calibration gases**

ANNEX A

BRIEF REVIEW OF THE PROPERTIES OF IDEAL AND NON-IDEAL GASES

A.1 DEFINITION OF AN IDEAL GAS

A perfect or ideal gas is a non-liquefiable gas whose molecules — of zero volume — do not interact with each other. It obeys the following relationship :

$$pV = nRT$$

where

p is the pressure of the gas, in pascals;

V is the volume of n moles of gas, in cubic metres;

T is the temperature of the gas, in kelvins;

R is the universal gas constant equal to 8,315 J/mol·K).

The principal causes of the non-ideality of the real gases are :

- steric hindrance : the molecules are not point masses;
- intermolecular forces (major reason) : the molecules, including the monoatomic ones, exert on each other certain forces of attraction which manifest themselves by a definite molar volume at a given temperature;
- electric forces : in the case of polar molecules;
- hydrogen bonds;
- quantum effects.

A.2 EQUATIONS OF STATE

A large number of equations have been proposed to describe the behaviour of real gases. In general, the more closely they represent reality, the more complex they are.

They may be conveniently classified according to the number of constants they contain. The following are as examples :

- 2 constants : Van der Waals, Berthelot, Dieterici, Redlich-Kwong;
- 4 constants : McLeod;
- 5 constants : Beattie-Bridgman;
- 8 constants : Benedict-Webb-Rubin, etc.

A.3 PRINCIPLE OF CORRESPONDING STATES

An examination of the phase diagrams of all gases reveals a great similarity in the shape of the isotherms. Examples of phase diagrams for carbon dioxide and ethylene are given in figures 2 and 3 respectively.

The principle of the corresponding states is based on this similarity.

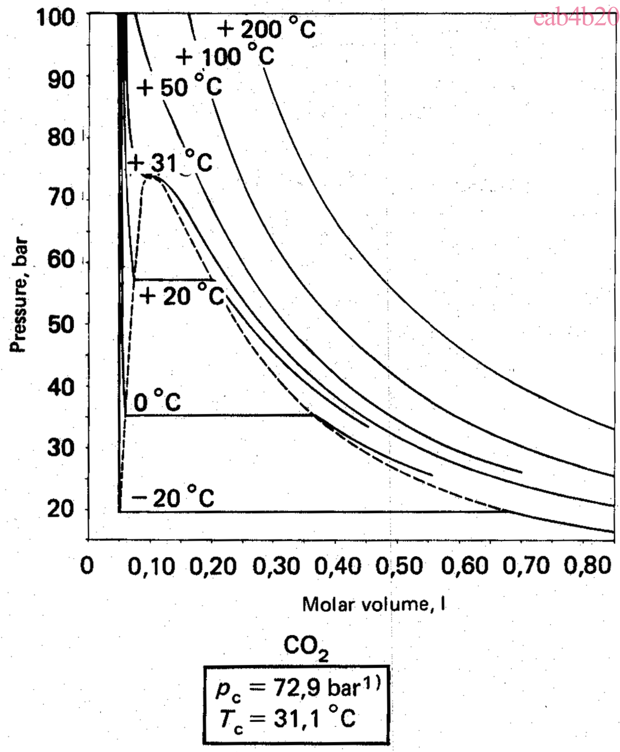


FIGURE 2 — **Phase diagram for carbon dioxide**

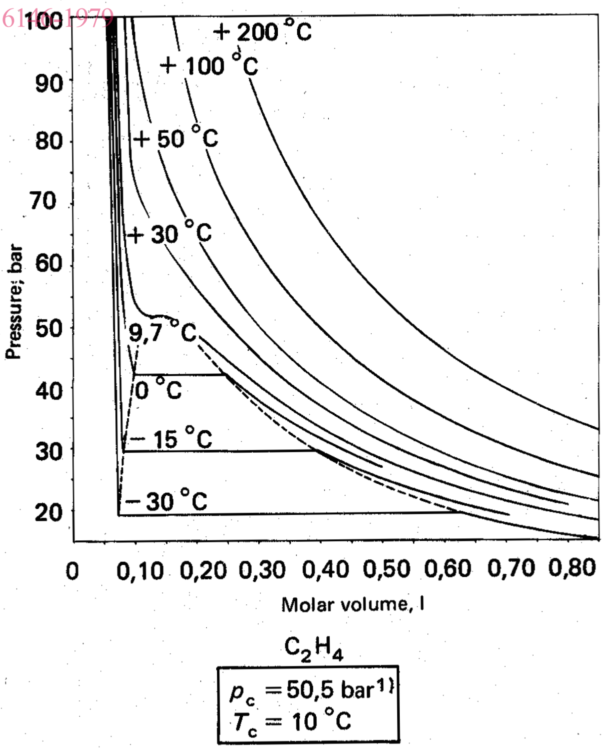


FIGURE 3 — **Phase diagram for ethylene**

---

1) 1 bar = 100 kPa

It is readily apparent that, for example, the 50 °C isotherms of these two gases are not directly comparable. In order to make such a comparison, reference is made to the coordinates of the critical point (p_c : critical pressure, T_c : critical temperature) by utilizing the reduced variables (p_r : reduced pressure, T_r : reduced temperature)

$$T_r = \frac{T}{T_c} \quad \text{and} \quad p_r = \frac{p}{p_c}$$

Two gases are in corresponding states when they have the same reduced temperature and pressure.

Example : Consider 1 mole of CO_2 (gas A) under the conditions

$$p = 90 \text{ bar}, \qquad T = 40 \text{ °C}.$$

It is desired to calculate the conditions of pressure and temperature of 1 mole of C_2H_4 (gas B) which is in a corresponding state :

$$\text{Gas A : } T_r = \frac{273 + 40}{273 + 31,1} = 1,02$$

$$p_r = \frac{90}{72,9} = 1,23;$$

$$\text{Gas B : } T = T_r T_c$$

$$= 1,02 \times (273 + 10) = 288,66 \text{ K } (= 15,6 \text{ °C})$$

$$p = p_r p_c$$

$$= 1,23 \times 50,5 = 62,12 \text{ bar.}$$

The two states :

$$CO_2 \left\{ \begin{array}{l} 90 \text{ bar} \\ 40 \text{ °C} \end{array} \right. \quad \text{and} \quad C_2H_4 \left\{ \begin{array}{l} 62,12 \text{ bar} \\ 15,6 \text{ °C} \end{array} \right.$$

are, therefore, corresponding states; they show the same deviation from ideality.

A.4 DEFINITION OF THE *Z*-COEFFICIENT

The *Z*-coefficient (also known as the Amagat constant) is simply defined by the relation :

$$Z = \frac{pV}{nRT}$$

The *Z*-coefficient, which is equal to 1 for ideal gases, takes account of the deviation from the ideal state. It permits the direct application of the law of ideal gas mixtures.

A.5 DETERMINATION OF THE *Z*-COEFFICIENT OF PURE GASES

A.5.1 Utilization of an equation of state

Numerous equations of state (see A.2) have been used for the calculation of the *Z*-factors. The convergence between various authors is generally sufficient to estimate the relative value of the systematic error incurred at less than 10^{-2}. Curves for some gases are given for guidance in annex D.

A.5.2 Utilization of the principle of corresponding states

The *Z*-coefficient is a function of the reduced parameters :

$$Z = f(T_r, p_r, Z_c)$$

where Z_c corresponds to the value of the *Z*-coefficient at the critical point. Lydersen, Greenkorn and Hougen have developed a relationship proposed by Meissner and Sefarian. The values of *Z*, at Z_c values ranging between 0,23 and 0,29, are given in the "Lydersen Tables" in annex E. This range of Z_c values covers most of the common applications.

A.6 LAWS OF IDEAL GAS MIXTURES

Under isothermal conditions :

A.6.1 Dalton's law

The total pressure of a mixture is equal to the sum of the partial pressures of the components of the mixture in a given volume.

If p_A, p_B and p_C are the partial pressures of the components A, B and C, then the total pressure p is :

$$p = p_A + p_B + p_C$$

A.6.2 Amagat's law

The total volume of a gas mixture at a given pressure is equal to the sum of the partial volumes of the components of the mixture.

If V_A, V_B and V_C are the partial volumes of the constituents A, B and C, then the total volume of the mixture is :

$$V = V_A + V_B + V_C$$

ANNEX B

CONVERSION OF A CONCENTRATION EXPRESSED IN TERMS OF A PRESSURE RATIO INTO A CONCENTRATION EXPRESSED IN TERMS OF A MOLE RATIO

This conversion requires allowance for the behaviour of real gases. The equations containing the *Z*-coefficient are commonly used because of their simplicity. Two preliminary choices are, however, indispensable :

- that of the *Z*-coefficient of the pure gases (see A.5);
- that of the rule of mixing best suited to the problem.

Three methods are available for this second choice.

NOTE — The different rules of mixing laid down in this annex are applicable to gases which are no more than slightly polar. In the case of polar gases, the incurred errors are much greater and difficult to quantify.

B.1 DALTON'S METHOD

If p_A, p_B and p_C are the pressures read after the introduction of the components A, B and C, then the pressures $p_A{}^*$, $p_B{}^*$ and $p_C{}^*$ exerted by these same gases, if they were ideal, are :

$$p_A{}^* = \frac{p_A}{Z_A}$$

(Z_A determined for the p_A pressure value)

and, as a first approximation :

$$p_B{}^* = \frac{p_B - p_A}{Z_B}$$

(Z_B determined for the ($p_C - p_A$) pressure value)

$$p_C{}^* = \frac{p_C - p_B}{Z_C}$$

(Z_C determined for the ($p_C - p_B$) pressure value)

The concentrations are expressed in mole fractions by the relation :

$$X_i = \frac{p_i{}^*}{\sum_{i=1}^{n} p_i{}^*}$$

The *Z*-coefficient of the mixture is equal to the weighted average of the various values of *Z* taken at the respective partial pressures :

$$Z\,(X_A + X_B + X_C) = X_A Z_A + X_B Z_B + X_C Z_C$$

This method can be applied with good accuracy in the case of mixtures prepared at low pressures ($p < 3$ bar). At high pressures, it is used only with components whose *Z*-coefficients are very different.

B.2 AMAGAT'S METHOD

Retaining the notations of the preceding clause, the corrected partial pressures of the components, A, B and C are now :

$$p_A{}^* = \frac{p_A}{Z_A}$$

(Z_A determined for $p_A + p_B + p_C$ pressure)

$$p_B{}^* = \frac{p_B - p_A}{Z_B}$$

(Z_B determined for $p_A + p_B + p_C$ pressure)

$$p_C{}^* = \frac{p_C - p_B}{Z_C}$$

(Z_C determined for $p_A + p_B + p_C$ pressure)

The mole fractions are also expressed by the relation :

$$X_i = \frac{p_i{}^*}{\sum_{i=1}^{n} p_i{}^*}$$

Amagat's correction is applicable with an accuracy of less than 5 % in the case of mixtures at low pressure ($p < 5$ bar). At high pressures, it proves to be better than Dalton's correction, particularly in the case of gases whose reduced temperature and pressure (T_r and p_r) are high.

B.3 METHOD OF PSEUDO-CRITICAL CONSTANTS

This method is a direct application of the principle of corresponding states. The gaseous mixture is considered as a pure fluid whose "pseudo-critical" constants are obtained by the rules of mixing.

The most frequently used rule of mixing is Kay's method. The pseudo-critical constants of the mixture are the weighted averages of the critical constants of each component.

$$T_{c_m} = \Sigma X_i T_{c_i}$$

$$p_{c_m} = \Sigma X_i p_{c_i}$$

$$Z_{c_m} = \Sigma X_i Z_{c_i}$$

(*X* is the mole fraction, though only as a first approximation; it is subtituted by the concentrations expressed in terms of pressure ratios.)

The change to the reduced variables :

$$T_{r_m} = \frac{T}{T_{c_m}} \quad \text{and} \quad p_{r_m} = \frac{p}{p_{c_m}}$$

and the use of Lydersen's tables (see annex E) makes it possible to determine the Z-coefficient of the mixture. The mole fractions are then calculated from the relation

$$X_i = \frac{p_i/Z_i}{p_m/Z_m}$$

where

p_i is the pressure of introduction of component i;

p_m is the total pressure of the mixture.

The limitations of the method are linked mainly to the use of Kay's rule. An accuracy of 2 to 5 % can be expected in the following region :

$$0{,}2 < \frac{T_{c_i}}{T_{c_j}} < 0{,}5 \quad \text{and} \quad p_{c_i} \approx p_{c_j}$$

where i and j relate to any two gases.

Outside these limits, the incurred error may be as large as 10 %, with the largest errors occurring at critical temperatures and pressures of the mixture close to unity.

NOTE — In the case of He, H_2 and Ne, the reduced parameters are obtained from the relationship

$$T_r = \frac{T}{T_c + 8} \quad , \quad p_r = \frac{p}{p_c + 8}$$

ANNEX C
EXAMPLES

C.1 BINARY MIXTURE OF CARBON DIOXIDE IN HYDROGEN

This mixture at 20 °C is such that :

$p_1 =$ 20 bar[1] after the introduction of CO_2

$p_2 =$ 100 bar after the introduction of H_2

Numerical data :

Z_{CO_2} at 20 bar = 0,87

Z_{H_2} at 80 bar = 1,05

$$CO_2 \left\{ \begin{array}{l} T_c = 304{,}2 \text{ K} \\ p_c = 72{,}9 \text{ bar} \\ Z_c = 0{,}274 \end{array} \right.$$

$$H_2 \left\{ \begin{array}{l} T_c = 33{,}3 \text{ K} \\ p_c = 12{,}8 \text{ bar} \\ Z_c = 0{,}304 \end{array} \right.$$

C.1.1 Conversion according to Dalton's method

$$p^*_{H_2} = \frac{80}{1{,}05} = 76{,}2 \text{ bar}$$

$$p^*_{CO_2} = \frac{20}{0{,}87} = 23{,}0 \text{ bar}$$

$$x_{CO_2} = \frac{23}{76{,}2 + 23} = \underline{23{,}2\ \%}$$

C.1.2 Conversion according to the method of pseudo-critical constants

Calculation of the critical parameters of the mixture :

$$T_{c_m} = (0{,}2 \times 304{,}2) + (0{,}8 \times 33{,}3) = 87{,}48$$

$$p_{c_m} = (0{,}2 \times 72{,}9) + (0{,}8 \times 12{,}8) = 24{,}82$$

$$Z_{c_m} = (0{,}2 \times 0{,}274) + (0{,}8 \times 0{,}304) = 0{,}298$$

Calculation of the reduced parameters of the mixture :

$$T_{r_m} = \frac{20 + 273}{87{,}48} = 3{,}35$$

$$p_{r_m} = \frac{100}{24{,}82} = 4{,}03$$

The ratio of these values in Lydersen's tables indicates a Z_m equal to 0,987.

Hence

$$x_{CO_2} = \frac{20 \times 0{,}987}{0{,}87 \times 100} = \underline{22{,}7\ \%}$$

C.1.3 Conversion according to Amagat's method

Not applicable since CO_2 is liquid at p = 100 bar.

NOTE — This example represents, in fact, a very unfavourable case, since the three modes of calculation are outside their range of application (pressure too high for Dalton's method and $\frac{T_{cH_2O}}{T_{cCO_2}}$ too low for Kay's rule).

The method of pseudo-critical constants will, however, be retained, but the molar concentrations will be known only with a relative accuracy of 5 to 10 %.

C.2 BINARY MIXTURE OF METHANE/NITROGEN

This mixture at 16 °C is such that

p_1 = 20 bar after the introduction of CH_4

p_2 = 50 bar after the introduction of N_2

Numerical data :

Z_{CH_4} at 20 bar = 0,963

Z_{CH_4} at 50 bar = 0,910

Z_{N_2} at 20 bar = 0,994

Z_{N_2} at 50 bar = 0,993

$$CH_4 \left\{ \begin{array}{l} T_c = 190{,}7 \text{ K} \\ p_c = 45{,}8 \text{ bar} \\ Z_c = 0{,}290 \end{array} \right.$$

$$N_2 \left\{ \begin{array}{l} T_c = 126{,}2 \text{ K} \\ p_c = 33{,}5 \text{ bar} \\ Z_c = 0{,}291 \end{array} \right.$$

C.2.1 Conversion according to Dalton's method

$$p^*_{CH_4} = \frac{20}{0{,}963} = 20{,}77 \text{ bar}$$

$$p^*_{N_2} = \frac{30}{0{,}994} = 30{,}18 \text{ bar}$$

$$x_{CH_4} = \frac{20{,}77}{20{,}77 + 30{,}18} = \underline{40{,}77\ \%}$$

C.2.2 Conversion according to Amagat's method

$$p^*_{CH_4} = \frac{20}{0{,}910} = 21{,}98 \text{ bar}$$

$$p^*_{N_2} = \frac{30}{0{,}993} = 30{,}21 \text{ bar}$$

$$x_{CH_4} = \frac{21{,}98}{21{,}98 + 30{,}21} = \underline{42{,}12\ \%}$$

---

[1] 1 bar = 100 kPa

C.2.3 Conversion according to the method of pseudo-critical constants

Calculation of the critical parameters of mixtures according to Kay's rule :

$$T_{c_m} = (0{,}4 \times 190{,}7) + (0{,}6 \times 126{,}2) = 152\ \text{K}$$

$$p_{c_m} = (0{,}4 \times 45{,}8) + (0{,}6 \times 33{,}5) = 38{,}42\ \text{bar}$$

$$Z_{c_m} = (0{,}4 \times 0{,}290) + (0{,}6 \times 0{,}291) \approx 0{,}290$$

Calculation of the reduced mixture parameters :

$$T_r = \frac{289}{152} = 1{,}90 \qquad p_r = \frac{50}{38{,}42} = 1{,}30$$

Lydersen's tables give $Z_m = 0{,}973$.

Hence the molar concentration of the methane :

$$X_{CH_4} = \frac{20 \times 0{,}973}{0{,}963 \times 50} = 40{,}42\ \%$$

NOTE — The method of pseudo-critical constants is in this case the most accurate since

$$\frac{T_{cN_2}}{T_{cCH_4}} = 0{,}66$$