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Gas analysis — Preparation of calibration gas mixtures using dynamic volumetric methods —

Part 6:
Critical orifices

Analyse des gaz — Préparation des mélanges de gaz pour étalonnage à l'aide de méthodes volumétriques dynamiques —

Partie 6: Orifices critiques

Reference number
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Foreword

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

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

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

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

ISO 6145-6 was prepared by Technical Committee ISO/TC 158, *Analysis of gases*.

This second edition cancels and replaces the first edition (ISO 6145-6:1986), which has been technically revised.

ISO 6145 consists of the following parts, under the general title *Gas analysis — Preparation of calibration gas mixtures using dynamic volumetric methods*:

— *Part 1: Methods of calibration*

— *Part 2: Volumetric pumps*

— *Part 4: Continuous injection method*

— *Part 5: Capillary calibration devices*

— *Part 6: Critical orifices*

— *Part 7: Thermal mass-flow controllers*

— *Part 9: Saturation method*

— *Part 10: Permeation method*

Diffusion will be the subject of a future Part 8 to ISO 6145. Part 3 to ISO 6145, entitled *Periodic injections into a flowing gas*, has been withdrawn.

Introduction

This part of ISO 6145 is one of a series of standards that present various dynamic volumetric methods used for the preparation of calibration gas mixtures.

Gas analysis — Preparation of calibration gas mixtures using dynamic volumetric methods —

Part 6:
Critical orifices

1 Scope

This part of ISO 6145 specifies a method for the continuous production of calibration gas mixtures, containing two or more components, from pure gases or other gas mixtures by use of critical orifice systems. By selection of appropriate combinations of orifices and with the use of pure gases, the volume fraction of the calibration component in the calibration gas mixture can be varied by a factor of 10^4. Additionally, it can be changed by a factor of 10^2 by changing the initial pressures in the orifice systems. The uncertainty of the method depends mainly upon the flow calibration method and the variations in temperature and outlet pressure. The relative expanded uncertainty in the volume fraction obtainable for a binary mixture (at a coverage factor of 2) is 3 %.

If pre-mixed gases are used instead of pure gases, much lower volume fractions can be obtained (see Annex A). The mass flow rates or volume flow rates, from which the mass or volume fractions are determined, can be calculated and can be independently measured by a suitable method given in ISO 6145-1.

The merits of the method are that multi-component mixtures can be prepared as readily as binary mixtures if the appropriate number of orifices is utilized, and that a large quantity of calibration gas mixture can be prepared on a continuous basis. The range of flow rates can be from several millilitres per minute to approximately 10 l/min.

Although particularly applicable to preparation of gas mixtures at barometric pressure, the method also provides a means of preparation of calibration gas mixtures at pressures above barometric pressure.

Annex B gives practical hints on the use of the method.

2 Normative references

The following referenced documents are indispensable for the application 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 6143, *Gas analysis — Comparison methods for determining and checking the composition of calibration gas mixtures*

ISO 6145-1, *Gas analysis — Preparation of calibration gas mixtures using dynamic volumetric methods — Part 1: Methods of calibration*

3 Principle

When passed through a critical orifice at increasing upstream pressure p_1, the volume flow rate of gas passing through the orifice will increase. When the ratio of the gas pressure upstream p_1 and the gas pressure downstream of the orifice p_2 has reached a critical value, on further increase of p_1 the volume flow rate of the gas becomes independent with respect to p_2.

For a given gas, and at constant temperature the critical pressure ratio is:

$$\left(\frac{p_2}{p_1}\right)_{\text{crit}} = \left(\frac{2}{\gamma + 1}\right)^{\frac{\gamma}{\gamma-1}} \tag{1}$$

where γ is the ratio of the molar heat capacities of the gas at constant pressure and at constant volume.

For monatomic, diatomic and triatomic gases, this critical pressure ratio is approximately 0,5.

Orifice systems which are operated at pressure ratios p_2/p_1 less than $(p_2/p_1)_{\text{crit}}$ are termed “critical orifices”. Use of such systems provides a means of maintaining constant flow rates of gases. In actual practice it is convenient to arrange the system so that p_2 is equal to the prevailing barometric pressure.

To prepare calibration gas mixtures, the complementary gas is supplied at known flow rate, from a critical orifice, to meet the calibration component emerging from another critical orifice. The mixture is then allowed to pass along a mixing tube, at the end of which the flow rate is measured by a suitable method as given in ISO 6145-1. Since the volume flow rate of the calibration component remains the same whether or not the complementary gas is flowing, it can be measured after the flow of complementary gas has been stopped. The concentration of the calibration gas mixture is calculated from the two measured critical flow rates.

4 Application to preparation of gas mixtures

4.1 Description of the orifice system and the experimental procedure

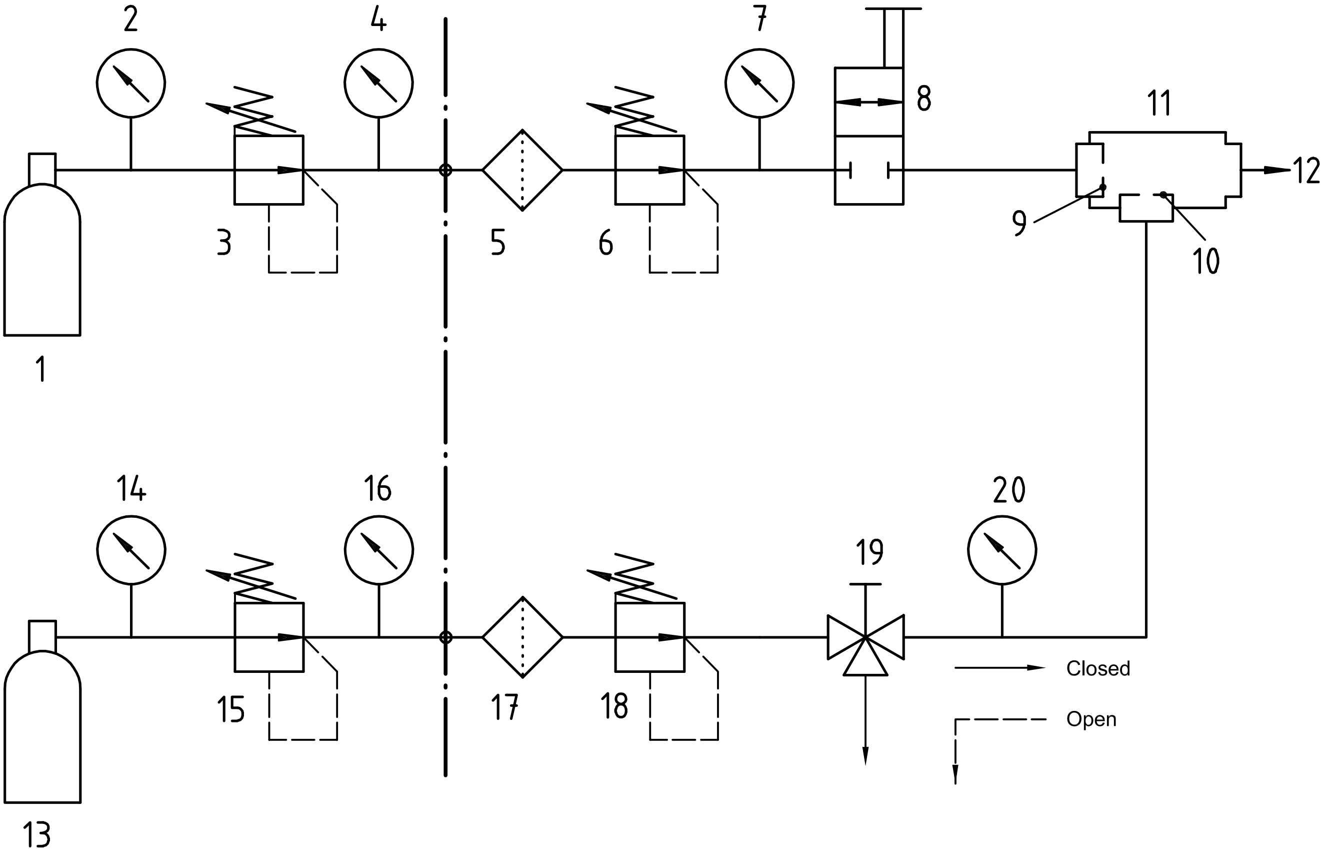
A schematic diagram of the arrangement for preparation of binary mixtures is shown in Figure 1.

In Figure 1, the orifices 9 and 10, respectively, for the complementary gas and the calibration component to be added are mounted in the orifice system (11). Cylinders 1 and 13, respectively, contain the complementary gas and the other gaseous component, and are connected to the mixing system via pressure-reducing valves (3 and 15) and metallic filters (5 and 17), which provide protection against contamination. In each of the lines, and upstream of the filters, are a pressure-reducing valve and a pressure gauge. A shut-off valve (8) is provided in the complementary gas line and a venting valve is included in the other line.

To operate the gas-mixing system, the valves of the gas cylinders are opened and the readings on the pressure gauges 4 and 16 are adjusted, each to a value approximately 200 kPa (2 bar) above the values anticipated at pressure gauges 7 and 20 respectively.

The pressure regulators (6 and 18) are opened so that the complementary gas and the calibration component flow through the respective orifices. The flow of complementary gas is then stopped by closing the shut-off valve 8. The other line is then flushed with the calibration component by repeated opening and closure of the venting valve 19. Valve 19 is then closed and pressure regulator 18 is adjusted so as to set the pressure at gauge 20 to the value necessary to produce the required flow rate (see below). The flow rate is then measured, by one of the methods given in ISO 6145-1, at outlet 12 of the orifice system (11).

The shut-off valve 8 is then opened and pressure regulator 6 is adjusted to set the pressure indicated on pressure gauge 7 to the value necessary to produce the required flow rate. The combined flow rates of the complementary gas and the calibration component are then measured by a suitable method according to ISO 6145-1.



Key

1	pressure cylinder (complementary gas)
2	pressure gauge (inlet pressure)
3	pressure-reducing valve
4	pressure gauge (delivery pressure)
5	filter
6	pressure regulator
7	pressure gauge
8	shut-off valve
9	orifice (complementary gas)
10	orifice (calibration component)
11	orifice system
12	exit for calibration gas mixture
13	pressure cylinder (calibration component)
14	pressure gauge (inlet pressure)
15	pressure-reducing valve
16	pressure gauge (delivery pressure)
17	filter
18	pressure regulator
19	vent valve
20	pressure gauge

Figure 1 — Preparation of calibration gas mixtures with a critical orifice system

4.2 Area of validity

The method is applicable to preparation of mixtures of non-reacting species, i.e. those which do not react with any material of construction of the flow path within the orifice system or the ancillary equipment. Particular care shall be exercised if the method is considered as a means of preparation of gaseous mixtures that contain components which form potentially explosive mixtures in air. Steps shall be taken to ensure that the apparatus is safe, for example by means of in-line flame arrestors in addition to the items listed in 4.1 (unless the in-line metallic filters already present are in fact approved sintered metal flame arrestors). This is of particular importance in this method because the gases in the dilution system are at pressures appreciably above the prevailing barometric pressure.

The method is not absolute and each orifice system shall be calibrated for the particular gas for which it is to be used. This is necessary because the formula for the volume flow rate of a gas includes the molar mass.

4.3 Operating conditions

The general precautions common to all dynamic techniques of preparation shall be observed. It is essential that attention is paid to the materials used in construction of the flow system. Only materials of low porosity and which are non-adsorbing are suitable. The pipe work shall be clean and all joints secure.

5 Calculation of operating parameters and results

5.1 Selection of suitable orifice systems

The volume flow rate of a gas through an orifice at $p_2 \leqslant 0{,}5 p_1$ is given by:

$$q_0 = \frac{p_1}{p_\mathrm{n}} \sqrt{\frac{T_\mathrm{n}}{T_1}} \cdot A \sqrt{\frac{R T_\mathrm{n}}{M}} \cdot \sqrt{\gamma \left(\frac{2}{\gamma + 1} \right)^{\frac{\gamma+1}{\gamma-1}}} \qquad (2)$$

where (in the appropriate units)

q_0	is the volume flow rate of the gas under normal conditions;
p_n	is the standard atmospheric pressure (101,325 kPa);
T_n	is the normal temperature (273,15 K);
p_1	is the pressure of the gas upstream of the orifice;
T_1	is the upstream temperature of the gas;
R	is the universal gas constant $[8{,}314\,510$ J/(mol·K)$]$;
M	is the molar mass of the gas, in grams per mole;
γ	is the ratio of the molar heat capacities of the gas at constant pressure and at constant volume;
A	is the cross-sectional area of the orifice;
p_2	is the pressure of the gas downstream of the orifice.

At a constant temperature, T_1, Equation (2) can be simplified to:

$$q_0 = \mathrm{D} \cdot d^2 \cdot M^{-\frac{1}{2}} \cdot p_1 \qquad (3)$$

where

d is the diameter of the orifice;

D is a constant.

For polyatomic gaseous molecules, the ratio of the molar heat capacities, γ, is calculated from the known value of C_p, the molar heat capacity at constant pressure, and the value of C_V, the molar heat capacity at constant volume calculated from the relationship $C_p - C_V = R$. The value for D can then be calculated.

When the constant multiplier has been evaluated, Equation (3) is applied to calculate the diameter of the orifice to deliver the required flow rate of a gas of molar mass, M, at upstream pressure p_1.

5.2 Calculation of volume fraction

The volume fraction, φ_A, in the calibration gas mixture, is calculated from the equation:

$$\varphi_\mathrm{A} = q_\mathrm{A} / (q_\mathrm{A} + q_\mathrm{B}) \qquad (4)$$

in which q_A and q_B are the volume flow rates of the calibration component and the complementary gas, respectively.

When the flow rates are determined with reference to ISO 6145-1, due consideration shall be given to the uncertainty associated with the method selected.

5.3 Sources of uncertainty

5.3.1 General

The volume flow rate of a gas through an orifice depends on the pressure upstream from the orifice and the temperature at the orifice. It is essential, therefore, to use good-quality pressure-reducing valves and pressure regulators in order to maintain the upstream pressure at a constant value. The coefficient of expansion of the calibration component and that of the complementary gas will differ slightly, depending upon the respective degrees of departure from ideality. However, to a very good approximation, small changes in temperature will cause negligible change in the flow rate ratio, provided that the temperature is the same at each orifice.

5.3.2 Downstream pressure

The thermodynamic treatment, which leads to the independence of the volumetric flow rate with respect to the downstream pressure, is not completely realized in actual practice, i.e. in the case of real orifices. At supercritical flow, therefore, the downstream pressure (p_2) still has some influence that can result in changes in volumetric flow rate if fluctuations in p_2 occur. The characteristic curve relating flow rate to pressure depends on the geometry of the orifice and the flow direction through the orifice. For measurements of the highest accuracy, this curve shall be established by calibration.

5.3.3 Temperature differentials

The orifice system would normally be arranged so that the temperature at each orifice is identical. However, if there is a temperature difference between the two components to produce a binary mixture, the volume flow rate of one shall be corrected by application of the coefficient of thermal expansion of the gas. For an ideal gas the coefficient is 0,003 661 per kelvin, and this value can be applied for real gases to a very good approximation for small differences in temperature between the gaseous components.

The following example demonstrates the magnitude of the errors which may be involved. The coefficient of thermal expansion of carbon dioxide is 0,003 72 per kelvin; that of hydrogen is 0,003 66 per kelvin. The method is employed to prepare a mixture of hydrogen and carbon dioxide at 293 K in which the volume fractions are to be 0,5. However, there is a temperature differential such that the hydrogen is at 292 K and the carbon dioxide is at 294 K. The volume fraction of hydrogen in the mixture at 293 K is $1{,}003\,66 \times 0{,}5 = 0{,}502$ and that of carbon dioxide is $(1 - 0{,}003\,72) \times 0{,}5 = 0{,}498$. The error in the volume fraction for a 2 K temperature differential is therefore 0,4 % relative. This demonstrates that it is necessary to maintain the component gases at the same temperature as each other or to apply corrections to the volume flow rates if there is a temperature differential.

5.3.4 Inefficient mixing

Another possible source of error is inefficient mixing of the calibration component and the complementary gas. A check of the efficiency of mixing is provided by verification of the volume (or mass) fraction by means of the comparison method (see ISO 6143).

5.4 Uncertainty of volume fraction

The uncertainty of the volume fraction of the calibration component in the calibration mixture, at constant temperature and pressure, can be estimated from the separate uncertainties in the flow rates of the calibration component and the complementary gas.

The volume fraction of component A is given by Equation (4).

The relative expanded uncertainty in φ_A is then given by:

$$\frac{U(\varphi_\mathrm{A})}{\varphi_\mathrm{A}} = \left[\frac{2q_\mathrm{B}}{q_\mathrm{A} + q_\mathrm{B}}\right] \left[\left(\frac{u(q_\mathrm{A})}{q_\mathrm{A}}\right)^2 + \left(\frac{u(q_\mathrm{B})}{q_\mathrm{B}}\right)^2\right]^{\frac{1}{2}} \tag{5}$$

The derivation of this formula is presented in Annex C of ISO 6145-7:2001[1]. The r.m.s. sum of the relative standard uncertainty contributions is multiplied by the coverage factor $k = 2$ to give a coverage probability of approximately 95 %.

The standard uncertainties $u(q_\mathrm{A})$ and $u(q_\mathrm{B})$ in the respective flow rates are obtained by reference to ISO 6145-1 for the selected method of flow calibration.

This estimate of the relative uncertainty in the composition rests entirely on the uncertainties in measurements of flow rates. The other factor to be taken into account is the efficiency of mixing. To check the effectiveness of a mixing system to provide a homogeneous calibration gas mixture, mixtures shall be prepared by the method as described and the compositions shall be checked by the comparison method of ISO 6143. This procedure also identifies bias from other sources and establishes traceability against standard mixtures.

Annex A
(informative)

Premixed gases for preparation of mixtures of high dilution

A.1 Calculation of results

If premixed gases are used instead of pure gases, mixtures of higher dilution can be prepared. Calculation of results is then as follows.

The volume fraction of component A in the final calibration gas mixture is given by:

$$\begin{aligned}\varphi_\mathrm{A} &= \frac{\varphi'_\mathrm{A} q_\mathrm{M} + \varphi''_\mathrm{A} q_\mathrm{B}}{q_\mathrm{M} + q_\mathrm{B}} \\ &= \frac{\varphi'_\mathrm{A} q_\mathrm{M} + \varphi''_\mathrm{A} q_\mathrm{B}}{q_\varphi}\end{aligned} \tag{A.1}$$

where

φ'_A is the volume fraction of A in the premixed gas;

φ''_A is the volume fraction of A in the complementary gas B (this will normally be zero);

q_M is the volume flow rate of the premixed gas;

q_B is the volume flow rate of the complementary gas B;

q_φ is the volume flow rate of the calibration gas mixture.

NOTE $q_\varphi = q_\mathrm{M} + q_\mathrm{B}$ only if there is no volume change on mixing.

A.2 Uncertainty of volume fraction

It is necessary to take into account the uncertainties of the volume flow rates and the uncertainties of the volume fractions of the component in the premixed gas and also in the complementary gas (if relevant). Normally the complementary gas will not contain the calibration component.

For the case in which the complementary gas does not contain the calibration component A:

$$\varphi_\mathrm{A} = \frac{\varphi'_\mathrm{A} q_\mathrm{M}}{q_\mathrm{M} + q_\mathrm{B}} \tag{A.2}$$

and the relative expanded uncertainty in the volume fraction (φ_A) is given by:

$$\frac{U(\varphi_\mathrm{A})}{\varphi_\mathrm{A}} = \frac{2 q_\mathrm{B}}{q_\mathrm{B} + q_\mathrm{M}} \left[\left(\frac{u(q_\mathrm{M})}{q_\mathrm{M}} \right)^2 + \left(\frac{u(q_\mathrm{B})}{q_\mathrm{B}} \right)^2 + \left(\frac{q_\mathrm{M} + q_\mathrm{B}}{q_\mathrm{B}} \right)^2 \left(\frac{u(\varphi'_\mathrm{A})}{\varphi'_\mathrm{A}} \right)^2 \right]^{\frac{1}{2}} \tag{A.3}$$

The derivation of this formula is presented in Annex C of ISO 6145-7:2001[1]. The r.m.s. sum of the standard uncertainty contributions is multiplied by the coverage factor $k = 2$ to give a coverage probability of approximately 95 %.

The uncertainties in all of the flow rates are obtained with reference to ISO 6145-1 for the selected method of flow calibration.

Annex B
(informative)

Practical hints

B.1 General

The complete flow system should be clean and free from particulates.

Pressure regulators and associated pipe work should be dedicated for use with specific gaseous components.

Shut-off valves should be located between pressure regulators and critical orifices in order to ensure that there is no leakage past the regulators.

All dimensions of the flow paths and the materials of construction should be carefully selected so that interaction with the gaseous components is minimized. In particular, pressure regulators should be suitable for the gases which they are to convey. GC-quality stainless steel should be used to convey reactive components. It is permissible for non-reactive complementary gases to be conveyed in plastics materials such as polyethylene or polytetrafluoroethylene, provided that all components and connections are suitable for use at the pressures within the system. If there is any risk of adsorption, however, stainless steel should be used.

At the commencement, the pipe work for the active component should be purged with the component concerned. A short period is satisfactory in the case of the pure gas or premixed gas at the higher concentrations, but several hours are necessary for the more dilute premixed gases (below 10^{-4} by volume).

In event of short interruption in the analyser calibration procedure, conveyance of the gases should not be stopped and, if connecting tubes are removed, they should be adequately sealed against contamination.

NOTE Liquefaction of a gas may occur (Joule-Kelvin effect) on expansion through an orifice. It is necessary to bear this in mind in the use of this method of gas mixing if any of the components are readily condensable, and to be sure of the suitability of the method for the particular gas mixture which is to be prepared. If, however the temperature is maintained at the ambient temperature 20 °C or above that value, and there is negligible temperature difference between the orifices (see 5.3.3), there should be no additional uncertainty in the final composition.

B.2 Construction of the calibration rig

As regards the orifices themselves, it is convenient to maintain several systems equipped with pairs (or sets) of orifices for the calibration component and the complementary gas. The possibility of contamination is reduced by leaving these orifices in the mixing device. For all of them, the characteristic curve which relates the volumetric flow rate to the inlet pressure can be predetermined.

In the use of this gas mixing method, upstream pressures of between 300 kPa and 600 kPa (3 bar and 6 bar) are recommended.

With the equipment outlined below (refer also to 4.1 and Figure 1), the relative reproducibility of the volumetric flow rate through an orifice has been shown experimentally to be within $1{,}7 \times 10^{-3}$.

a) Pressure-reducing valves and pressure gauges: delivery pressure range 150 kPa to 2 000 kPa (1,5 bar to 20 bar).

b) Pressure regulators: to maintain the pressure upstream of each orifice at a constant value.

c) Absolute pressure gauges: range 0 kPa to 700 kPa (0 bar to 7 bar).

d) Measurement uncertainty 0,07 % full scale:
   - response sensitivity 0,01 %;
   - maximum hysteresis 0,05 %;
   - maximum temperature coefficient 0,002 % per kelvin.

e) Flow rate determination to a measurement uncertainty:
   - 0,2 % within the range 0,1 ml/min to 3,0 ml/min;
   - 0,5 % within 3,0 ml/min to 30 ml/min for the calibration component, and to 0,2 % within the range 10 l/h to 600 l/h for the calibration gas mixture.

f) Orifice diameter range: 5 μm to 1 000 μm.

NOTE The above technical data are quotations from the specifications of the manufacturers of the respective instruments, as given in Reference [2].

B.3 Some relevant physical properties (see 5.1)

B.3.1 Values of C_p for some common gases with more than two atoms per molecule

Gas	C_p [**J/(mol·K)**]
NO_2	37,3
SO_2	39,9
C_3H_8	70 (293 K)
	72,8 (298 K)
NH_3	35,8
CO_2	37,3

B.3.2 Coefficients of volume expansion of some gases (see 5.3.2)

The values shown below are mean coefficients at 100 kPa (1 bar) over the temperature range 273 K to 373 K.

H_2	$3,66 \times 10^{-3}$ K^{-1}
N_2	$3,68 \times 10^{-3}$ K^{-1}
CO_2	$3,72 \times 10^{-3}$ K^{-1}

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[1] Corrected and reprinted in 1995.

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