THE SAFE PREPARATION OF GAS MIXTURES

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Asia Industrial Gases Association
N0 2 Venture Drive, #22-28 Vision Exchange, Singapore 608526
Tel: +65 67055642 Fax: +65 68633379
Internet: http://www.asiaiga.org | LinkedIn Profile: https://www.linkedin.com/company/asiaigaorg

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As part of a program of harmonisation of industry standards, the Asia Industrial Gases Association (AIGA) has published AIGA 047, "*The Safe Preparation of Gas Mixtures", jointly* produced by members of the International Harmonization Council and originally published by the European Industrial Gases Association (EIGA) as Doc 039, "*The Safe Preparation of Gas Mixtures".*

This publication is intended as an international harmonised publication for the worldwide use and application by all members of the International Harmonisation Council whose members include the Asia Industrial Gases Association (AIGA), Compressed Gas Association (CGA), European Industrial Gases Association (EIGA), and Japan Industrial and Medical Gases Association (JIMGA). Each association's technical content is identical, except for regional regulatory requirements and minor changes in formatting and spelling.

ATTENTION IS DRAWN TO THE NEED TO COMPLY WITH ALL NATIONAL REGULATIONS WHICH AFFECT THE PREPARATION OF GAS MIXTURES

ASIA INDUSTRIAL GASES ASSOCIATION
No-2 Venture Drive,# 22-28 Vision Exchange, Singapore 608526
Tel: +65 67055642 Fax: +65 68633307
Internet: http://www.asiaiga.org LinkedIn Profile: https://www.linkedin.com/company/asiaigaorg

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Note: Technical changes from the previous edition are underlined

1 Introduction

For many years, the gas industry has produced a wide range of gas mixtures. All gas mixing operations require the normal safety procedures, practices and controls that are followed when filling standard industrial gases. Additional controls are required when mixing potentially incompatible gases. For this reason, great care is necessary during the preparation of such mixtures to ensure that no uncontrolled reactions take place.

Regulations and procedures for gas mixing vary in some details from one manufacturer to another, however, they should always be based on the same safety principles. Details concerning the safe manufacture of oxidant-fuel mixtures are described in AIGA 058, *Safe Preparation of Compressed Oxidant-Fuel Gas Mixtures in Cylinders* [1].[1]

Manufacturers of gas mixtures for medical use should also refer to AIGA 023, *Good Manufacturing Practice Guide for Medicinal Gases* [2].

2 Scope and Purpose

The sole aim of this publication is to set out the basic requirements to ensure that gas mixtures are manufactured safely. This publication is not intended to be a manual on how to manufacture gas mixtures.

3 Definitions

For the purpose of this publication, the following definitions apply.

3.1 Publications terminology

3.1.1 Shall

Indicates that the procedure is mandatory. It is used wherever the criterion for conformance to specific recommendations allows no deviation.

3.1.2 Should

Indicates that a procedure is recommended.

3.1.3 May

Indicates that the procedure is optional.

3.1.4 Will

Is used only to indicate the future, not a degree of requirement.

3.1.5 Can

Indicates a possibility or ability.

3.2 Technical definitions

3.2.1 Cylinder

Any transportable receptacle that can be filled with gas under pressure.

[1] References are shown in bracketed numbers and are listed in order of appearance in the reference section

3.2.2 Filling ratio (Also known as filling degree or filling density)

Ratio of the mass of gas to the mass of water at 15 °C (59 °F) that would fill completely a pressure receptacle fitted ready for use, see ADR [3].

NOTE—In other jurisdictions, the filling ratio may be defined slightly differently.

The filling ratio (f) is expressed as the ratio: (M/C),

Where:

M = mass of gas filled (kg)

C = cylinder water capacity (L)

3.2.3 Hazop

Technique to identify and assess potential hazards that could arise during the operation of plant or equipment. A hazop study is carried out to assess the potential effects of various malfunctions of the equipment or plant (e.g., reverse flow, excessive temperature or pressure, etc.).

3.2.4 Hygroscopic

Substance that has an affinity for water. Many acid gases are hygroscopic (e.g., hydrogen chloride) and, when in the wet state, are normally much more reactive with materials of construction.

3.2.5 Liquefied gas

Gas which when packaged under pressure for carriage is partially liquid at temperatures above –50 °C (–58 °F).

A distinction is made between:

- High pressure liquefied gas—a gas with a critical temperature above –50 °C (–58 °F) and equal to or below 65 °C (149 °F); and
- Low pressure liquefied gas—a gas with a critical temperature above 65 °C (149 °F).

3.2.6 Intermediate analysis

Analysis carried out part-way through the process of filling a gas mixture into a cylinder (or cylinders). Such an analysis is normally carried out to confirm the concentrations (and sometimes the identities) of the components that have been filled before a subsequent component is added.

3.2.7 Passivation

Procedure that is applied where there is a possibility of a reaction between a reactive gas and the container or system into which it is going to be introduced. Passivation ensures that any reaction takes place under controlled conditions. Passivation may also be used to ensure the stability of a gas mixture. Passivation is usually carried out using a mixture containing the reactive gas diluted in an inert gas.

3.2.8 Premix

Gas mixture that is used as one of the supply gases during the filling of a gas mixture. The use of premixes can enable low concentration components to be filled accurately and can also eliminate any potential hazards when filling certain gas mixtures containing potentially incompatible components.

3.2.9 Written instructions

Work instructions that are printed out on a paper or available digitally on an electronic device such as personal computer or tablet.

4 Principles of safe gas mixing

This section sets out the basic principles that shall be followed to ensure gas mixtures are produced safely.

4.1 Principle 1: Written instructions shall be provided

Gas mixtures shall only be filled in accordance with written and approved instructions. Normally the instructions issued will comprise operating procedures for the plant and equipment and specific instructions for each gas mixture to be prepared.

4.2 Principle 2: Equipment and facilities shall be properly designed

Gas mixtures shall only be prepared in properly equipped and approved facilities where provisions have been made for:

- Pressure and material compatibility of filling equipment with the intended mixtures;
- Adequate segregation of filling flammable and oxidant gases and other potentially incompatible components to clearly defined areas;
- Prevention of feed-back of gas from filling systems into supply gas systems; and
- Safe and environmentally responsible disposal of waste gases. AIGA 083, *Disposal of Gases* gives further detailed information [4].

4.3 Principle 3: Written instructions shall be prepared by competent staff using recognised data

Gas mixing instructions shall be prepared by trained and competent staff that check for:

- availability of recognised data;
- safety of the proposed method of manufacture and the final mixture;
- unsafe situations that could arise from the liquefaction (condensation) of components during and after mixing;
- quantity of product versus cylinder size (particularly with respect to liquefied gas mixtures, to ensure that the cylinder is not over-filled); and
- tolerance requirements for safe mixing.

4.4 Principle 4: Personnel shall be trained

Personnel engaged in gas mixing shall be given training based on written instructions covering:

- all aspects of preparing gas mixtures;
- key characteristics of the gases being handled and the safety requirements when dealing with them;
- recognition and mitigation of the hazards during mixture preparation that is found to be unsafe;

- protective clothing and equipment; and

- safety rules, emergency, and first-aid procedures.

The training shall be properly recorded, updated regularly, and competency assessed and confirmed.

4.5 Principle 5: Intended cylinder content shall be identified before filling

Before any cylinder is filled, it shall be clearly identified with the names and respective nominal concentrations of the intended mixture components (or the mixture registered trade name where appropriate). Alternative methods of identification that give an equivalent level of safety may be used. The content and status of the container during the production process shall also be recorded.

4.6 Principle 6: Supply gases and cylinders shall be controlled

There shall be adequate controls to ensure that:

- only the intended gases are used to prepare gas mixtures; and

- cylinders are suitable for the mixture, properly prepared, and free of any contaminants that can affect the safety of the filling process and/or the intended use of the mixture.

4.7 Principle 7: Facilities and procedures shall be audited

All operational gas mixing facilities and procedures shall be audited regularly for compliance with the previous six principles, 4.1 to 4.6.

5 Feasibility and classification of gas mixtures

There are more than 100 commonly available liquefied and permanent gases and a large number of liquids whose vapours are used in the formulation of gas mixtures. Gas mixtures can contain any number of components at almost any concentration, provided they are safe and technically feasible to produce. Hence, the potential range of available gas mixtures is almost infinite. This section gives basic guidance on the types of gas mixtures produced and the constraints that may be applicable to their manufacture.

5.1 Gas mixture availability constraints

The main constraints on the availability of gas mixtures are concerned with:

- Safety—The gas industry will not manufacture any gas mixture that could compromise the integrity of the cylinder, valve, dip tube, or filling system; and

- Technical feasibility—The physical and chemical properties of some mixture components have a limiting effect on what can be practicably manufactured (e.g., a very low vapour pressure can limit the concentration of the component and the final filling pressure of the gas mixture).

5.2 Gas mixture categories

Generally, gas mixtures can be grouped into two broad categories:

- Standard gas mixtures—those that are filled repeatedly on a large scale. Normally these are relatively simple, containing a small number (typically two or three) common standard gas components with filling and analytical tolerances that are not critical; and

- Special mixtures—those that are filled on a smaller scale than standard gas mixtures. These mixtures are frequently more complex than standard gas mixtures.

6 Gas mixing instructions

Gases and vapours may be mixed in any combinations at any concentrations provided the mixture is technically feasible and safe, i.e., components are compatible with each other and with the cylinder and its valve, both during filling and after mixing. The purpose of this section is to set out the principles and controls necessary to ensure safe gas mixing instructions can be formulated and issued. Some additional guidance is given on possible gas mixture filling strategies.

6.1 General controls

Gas mixtures shall only be filled against written and approved procedures. Such procedures shall cover both the filling equipment to be used and the specific gas mixture to be prepared.

6.2 Mixture-specific manufacturing instructions

Instructions specific to the mixture to be filled shall include:

- details of the cylinder and valve and their preparation;
- components and quantities to be added and the sequence of addition;
- means and methods of measuring the components into the cylinder and the filling equipment to be used;
- any special constraints relating to the rate at which the components are to be added (e.g., to minimise temperature increases);
- method of mixing the components; and
- any intermediate analysis requirements (i.e., analysis to be carried out during the filling process to confirm the correct quantities of some components have been filled before the addition of other component[s]).

6.3 Personnel responsible for preparing & authorising gas mixing instructions

Such personnel shall have sufficient technical education and relevant experience to be able to fully understand the chemical, physical and engineering principles involved in the formulation of mixing instructions and their subsequent approval. There shall be a list of authorised personnel. Listed personnel should not be placed under undue production or commercial pressures whilst preparing and authorising gas mixing instructions. Such personnel shall work to formalised procedures and instructions and shall work and communicate closely with the personnel who design gas mixing facilities and who prepare gas mixtures.

6.4 Safety system

The safety system shall ensure that gases are not mixed without proper written and approved mixing instructions and that the integrity of both the filling system and the containers being filled are not compromised. The gas mixing instruction approval system shall take into account:

- Enquiry and quotation stage—to ensure that no commitment is given to prepare an unsafe mixture;
- Acceptance of order into processing system—to ensure that orders for unsafe mixtures are not accepted;
- Formulation of gas mixing instructions—to ensure that formulation is only undertaken by trained and authorised personnel;
- Approval of gas mixing instructions—to ensure approval of written instructions prior to issue to production (see 6.5); and

- Computer systems used to calculate and/or store gas mixing instructions—to ensure that non-approved instructions are not released for production use. Safeguards against keying errors shall be incorporated into the system.

6.5 Approval of gas mixing instructions

Gas mixing instructions may be formulated manually or with the aid of appropriate computer software and database(s). Such software and database(s) shall be validated as correct and secure. Once formulated, gas mixing instructions may be issued directly for use and/or may be stored in a computer file for subsequent issue. Where a computer file is used for the storage and issue of previously formulated gas mixing instructions, all entries into the file shall be checked to ensure there are no keying errors including checking units of component concentration and method of measurement during filling. There shall be no unauthorised modification of the file content.

Gas mixing instructions, whether formulated manually or with the aid of a computer shall be checked, before issue for use or entry into a computer file for subsequent use as follows:-

- All instructions—by at least one competent person (the blender can be the competent person); and

- Instructions for mixtures that contain potentially incompatible components—by at least one additional competent person. For compressed oxidant-fuel gas mixtures refer to AIGA 058 [1].

6.6 Adjustment of gas mixing instructions

The adjustment of existing gas mixing instructions shall be subject to the same rigorous controls as new instructions. They shall not be adjusted without the authorisations detailed in 6.5.

6.7 Adjustment of existing mixtures

When a gas mixture is found to be out of tolerance after analysis, it is sometimes practicable to adjust the composition of the mixture by addition of one or more of the mixture component gases. Before this operation is undertaken, written instructions shall be formulated. Where the mixture adjustment involves addition of a gas that is potentially incompatible with the existing mixture components, the mixture adjustment instructions shall be reviewed according to 5.1 and approved by a competent person who is accountable for safety.

6.8 Consideration of mixing methods

The methods generally available for the preparation of gas mixtures in cylinders are listed in the following sections, together with the considerations necessary for safe operation. Combinations of two or more of these methods may sometimes be used.

These methods are also described in ISO standards, see Section 11.

6.8.1 Static methods

In this method, the mixture is produced directly in the cylinder by adding measured quantities of each of the mixture components. Mixing of these components may not be instantaneous and concentration gradients can be present during and immediately after filling the cylinder. This shall be taken into account to ensure that no dangerous mixtures can exist during filling. There are three commonly used methods of measuring the quantities of mixture components into the cylinder during filling. It may be appropriate to use a combination of these methods to prepare some gas mixtures. These static methods are as follows:

- *Manometric or partial pressure method:* Mixture components are filled into the cylinder to calculated pressures. The calculated pressures shall take into account the component compressibility factors and shall ensure that unwanted component liquefaction does not occur during or after the preparation of the mixture;

- *Volumetric method:* Calculated volumes of mixture components are filled into the cylinder. These calculated volumes shall ensure that unwanted component liquefaction does not occur during or after the preparation of the mixture; and

- *Gravimetric method:* Calculated masses of mixture components are filled into the cylinder. These calculated masses shall ensure that unwanted component liquefaction does not occur during or after the preparation of the mixture.

6.8.2 Dynamic method

In this method, the mixture is produced prior to filling into the cylinder by blending the components dynamically at calculated flow-rates. Normally, the dynamic blend is made at low pressure and subsequently compressed into the cylinder. Care shall be taken to ensure that a dangerous blend cannot be made if the flow control system fails. Account shall be taken of temperature rises during compression and the compatibility of lubricants with the mixture being compressed.

6.9 Compatibility considerations

Gas mixtures shall only be prepared where the proposed components are compatible with each other and with the cylinder and valve at the concentrations and pressures to be encountered during and after mixing.

6.9.1 Cylinders and cylinder valves

The cylinder and cylinder valve shall be suitable for their intended service.

- Cylinders and cylinder valves shall be suitable for the operating pressure. Due account shall be taken of the possible developed pressure at the elevated temperatures that can be encountered in storage, transport, and use. This is particularly important in the case of liquefied gas mixtures. Also refer to ADR rules governing filling ratio and filling pressures [3];

- Cylinders and cylinder valve materials (e.g., body, seat & packing) shall be chemically compatible with the gases contained. Attention is drawn to the need for expert consideration of all gas, cylinder and valve compatibility issues. Refer to ISO 11114-1, *Gas cylinders — Compatibility of cylinder and valve materials with gas contents — Part 1: Metallic materials* and ISO 11114-2, *Gas cylinders — Compatibility of cylinder and valve materials with gas contents — Part 2: Non-metallic materials* [5, 6], or local regulations, if any. Examples of potential incompatibilities and other chemical compatibility issues that should be taken into account include but are not limited to:

    - Some halogens and halogenated compounds can be incompatible with aluminium cylinders. Ensure that the concentrations of halogens and halogenated compounds used in the mixture are compatible with the material of the cylinders used

    - High-stress steels can be susceptible to embrittlement, stress corrosion and other corrosion with certain gases such as hydrogen ammonia, carbon monoxide, hydrogen sulphide, some halogens, and halogenated compounds. See AIGA 065, *Avoidance of Failure of Steel Cylinders Containing CO and CO/CO2 Mixtures*, European Industrial Gases Association and EIGA Doc 100, *Hydrogen Cylinders and Transport Vessels* [7, 8], or local regulations, if any

    - Possible effect of any impurities that the gas can contain

    - Some gases are only compatible when dry. In these cases, both the gas and the cylinder shall be free of moisture

    - Where a gas is corrosive when wet, particularly if the gas is also hygroscopic, the valve design and material shall be such as to minimise the effect of corrosion on the valve operating mechanism.

- When changing from one gas or gas mixture service to another, cylinders shall be free of substances that can remain from previous service. Gases can normally be removed by evacuation and/or purging (in some cases, such operations are best carried out whilst baking the cylinder). Solid and liquid substances (such as possible reaction products) may require the cylinder to be taken out of service, cleaned, and inspected internally prior to refilling. Refer to ISO 11621:1997, *Gas cylinders — Procedures for change of gas service* or CGA C-10, *Guideline to Prepare Cylinders and Tubes for Gas Service and Changes in Gas Service* [9, 10]

- It could be necessary to passivate cylinders, valves and equipment before certain highly reactive gases (e.g., fluorine) are introduced for the first time. Passivation is intended to minimise the risk of a violent reaction between the gas and materials that the gas comes into contact with. It is normally carried out by slowly introducing the gas to the system, initially in a diluted form and at low pressure, to ensure that any reactions that are likely to take place do so under controlled conditions;

- Cylinders shall be periodically inspected and tested (except non-refillable cylinders). Periods between inspection and test and the extent of the inspection and pressure to which cylinders are tested are dependent on the gas contained, the cylinder design code, and the country where the cylinder is filled and/or used. Such details are normally defined in international and national regulations. Refer to ADR rules governing periodic inspection and test requirements; and

- Special attention shall be given to customer-owned cylinders with regards to the previous points.

6.9.2 Mixture components

When a mixture is proposed, the approved competent person shall seek evidence from in-house experimental data or published literature (e.g., the German TRGS 407 + Tätigkeiten mit Gasen – Gefährdungsbeurteilung or NOAA Expanded Chemical Reactivity Worksheet (CRW4) for determining chemical compatibility, past, present, and future) to establish component compatibility [11, 12]. Gas mixtures normally fall into one of the following categories:

- Mixtures of components that are compatible at all concentrations, pressures and temperatures that can be encountered - gas mixing instructions can be formulated and approved;

- Mixtures of potentially incompatible components, where the component compatibility data or evidence is available at conditions different to those to be encountered during mixing. In such cases, the data or evidence shall be interpreted, and safety margins applied according to the company procedures; and

- Mixtures of potentially incompatible components where the component compatibility data or evidence is not available or shows non-compatibility. In such cases, the mixtures should not be prepared without first determining that the mixture is safe. The policy for dealing with such cases should be defined in company procedures.

6.9.3 Safety margins

When establishing safety margins for the mixing of potentially incompatible components, considerations shall include the following:

- Availability and accuracy of data;

- Accuracy of control of the mixing operation;

- Detailed understanding of the hazards of potential reactions (e.g., explosion data, energy releases, pressure rise etc.). Mixtures with chemically unstable gases (e.g., acetylene) may be limited in pressure or concentration according to the CLP Regulation [13]; and

- Possibility that, under certain conditions, condensation of one or more of the components can occur and could give rise to the formation of dangerous mixtures in the gaseous phase or at the interface with the liquid phase.

6.10 Identification and labelling

The following shall be observed:

- Prior to filling—Cylinder shall be painted when required (e.g., cylinders containing medical gases), clearly and durably marked in accordance with all applicable regulations; and

- Prior to shipping—All cylinders shall be labelled in accordance with all applicable regulations.

7 Design and operation of gas mixing facilities

All safety and legal requirements relating to the handling, storage, filling, and maintenance of cylinders and filling systems for the various categories of pure gases also apply to gas mixtures. It is recommended that safety and operability risk assessments are carried out on all processes and procedures. This section sets out basic guidance and identifies key issues for consideration. Where hazards are identified that could be fatal or lead to very serious injury, these hazards shall be immediately eliminated prior to any other actions. Where elimination of the hazard is not possible, the system shall be designed to incorporate physical controls to reduce the risks to a practicable minimum. Reliance on the operator following a procedure shall be used where there is no feasible alternative, but key stages in the procedure shall be subjected to independent checking by another individual. Change management procedures shall be used to ensure changes in operational procedures are reviewed and risk assessed prior to implementation.

7.1 General requirements

Issues for consideration include but are not limited to the following:-

- Operating and storage areas:
    - Ventilation requirements
    - Segregation of filling areas
    - Provision of adequate emergency exits
    - Controlled access of personnel
    - Fire protection and firefighting equipment
    - Eye washes and safety showers where corrosive materials are handled
    - Hazardous area classification according to ATEX directive 2014/34/EU and compliance of electrical equipment in these areas [14]
    - Gas monitoring where toxic, flammable gases, or oxygen-enriched or depleted atmospheres are a potential hazard;
- Equipment:
    - Suitability of equipment, materials of construction, and pressure rating
    - Gas disposal systems

- Accuracy of all production and analytical instruments used in the preparation of gas mixtures shall be adequate for the purpose and documented
- Drawings and labelling
- Separate equipment for flammable-inert gas mixtures and for oxygen-inert gas mixtures should be considered to prevent the accidental production of oxidant-fuel mixtures

- Supply gases:
  - Separate inert gas supplies for flammable-inert gas mixtures and for oxygen-inert gas mixtures shall be considered to prevent the accidental production of oxidant-fuel mixtures. If separate inert gas supplies are not installed, alternative safeguards shall be in place, e.g., safeguards for prevention of backflow.
  - Adequate labelling on all gas supply pipelines and cylinders
  - Storage identification and stock rotation for supply cylinders
  - Confidence in the supply gas certification and freedom from potentially hazardous impurities (including premixes); and
- Control of cylinders:
  - Control of cylinders in the mixture filling areas (i.e., kept to a minimum)
  - Ensuring that polymerisable substances (such as ethylene oxide, diborane, and 1,3-butadiene) are stored in accordance with the supplier's instructions
  - Provision of leak testing full cylinders and filling systems Storage areas suitable for the different hazard classes of gases according to a risk assessment.

7.2 Specific requirements

In addition to the general requirements of 0, the following are given for guidance when designing and operating facilities associated with gas mixtures:

7.2.1 Incoming cylinder reception & inspection

Operators of gas mixing facilities should recognise the relative complexity that results from the multiplicity of gas mixture combinations. Cylinders shall be identified and segregated for subsequent residual gas disposal and cylinder maintenance (where appropriate). Adequate space for this activity shall be allocated.

7.2.2 Disposal of residual gases

Adequate facilities shall be available for the safe disposal or recovery of all residual gases likely to be encountered from both the gas mixing process and from cylinders returned by customers after use. Guidance concerning the provision of such facilities is given in AIGA 083 [4]. Facilities established for the manufacture of gas mixtures frequently handle a large range of mixture components. It is very important to have adequate controls in place to prevent the inadvertent mixing (in potentially hazardous concentrations) of inter-reactive gases or other materials in the gas disposal equipment. Examples where controls are needed include:

- To ensure that the contents of all cylinders assigned for disposal have been correctly identified;
- To ensure that there is no risk of mixing incompatible gases, such as flammable and oxidant gases, within the gas disposal equipment, which could give rise to an uncontrolled reaction;

- To ensure there are qualified, competent, and appropriately equipped personnel available to specify or carry out certain non-routine gas disposal operations. Examples of typical non-routine gas disposal operations include:

    - Where there is no suitable gas disposal equipment readily available. Such operations shall be assessed by a person who has appropriate chemical experience and who is able to make recommendations concerning the safe gas disposal method and the equipment that can be used

    - Where the content of the cylinder is unknown, possibly old and lacking in markings (see AIGA 083 [4])

    - Where the cylinder content can be potentially explosive, possibly as a result of back-feeding an incompatible material into the cylinder

- Non-routine gas disposal operations can be potentially fatal and shall be thoroughly risk assessed prior to beginning any disposal work; and

- Where in-house resources and facilities are not available, to ensure that cylinders are properly consigned to a licensed competent third party for gas disposal (provided the cylinders are in a safe condition for handling and transport).

7.2.3 Cylinder maintenance and preparation

In addition to the facilities that are normally required for the maintenance and preparation of cylinders for pure gases (such as those used for industrial gases) the following are likely to be required:

- facilities for a wide range of cylinder painting and labelling;

- additional specialised cylinder internal inspection and cleaning equipment;

- facilities for the storage and fitting of a wide range of cylinder valves; and

- additional and specialised cylinder internal drying equipment.

7.2.4 Design of gas mixing facilities

Gas mixing systems shall be designed by competent personnel with the relevant experience and knowledge to ensure that these systems are safe and effective. New cylinder filling manifold designs or modifications shall be reviewed and approved prior to the use of the system. Wherever possible these systems should be simple to operate with a logical layout of cylinder filling manifold to minimise potential operator errors. Key points for consideration in the design of the gas mixing facility include:

- Gas filling systems and filling areas should be segregated as far as is practicable to eliminate the risk of inadvertently mixing of incompatible gases;

- Sections 10 and 11 give reference sources of physical, chemical, flammability and oxidising properties for gas mixture components and can be used in conjunction with the appropriate SDS data to assess the compatibility of products;

- Where incompatible gases are being mixed, the provision of a designated system combined with strict operational controls is necessary. There shall be sufficient checks to ensure that the mixture components are correctly added (as specified on the gas mixing instruction). This is to ensure that there is no risk of a hazardous condition inside the cylinder being filled at any time during the filling process;

- Where flammable components are to be stored and filled, consideration shall be given to the following:
    - Equipment and protective systems intended for use in potentially explosive atmospheres. In Europe, according to the Directive 2014/34/EU concerning equipment and protective systems intended for use in potentially explosive atmospheres and according to the Directive 1999/92/EC on minimum requirements for improving the safety and health protection of workers potentially at risk from explosive atmospheres (ATEX) and all applicable local regulations [14, 15].
    - Earthing of cylinder filling manifolds and associated equipment
    - Sources of static discharge
    - Building ventilation
    - Flammable gas detection systems and alarms
    - Explosion relief of buildings;
- Where toxic components are to be stored and filled consideration shall be given to the following:
    - Toxic gas detection systems and alarms
    - Personal detectors and appropriate personal protective equipment (PPE)
    - Building ventilation;
- Vent lines from cylinder filling manifolds shall be installed to let any residual gas vent in a safe manner. Care shall be taken to ensure that vent lines are installed in a manner to avoid any reaction between incompatible products. The vent lines should be separated and have the facility to purge the lines with inert gas;
- Precautions should be taken to avoid the suck back of contaminants (oil, scrubber solutions, etc.) from vacuum systems into cylinder filling manifolds and cylinders. Vacuum pumps used in oxidant service should use an appropriate oxidant compatible lubricant. (e.g., fluorinated pump oils);
- Adequate provision shall be made to prevent back-feeding of partially filled cylinders into other filling systems or cylinders via supply, vent, and vacuum systems. This is particularly important where a common supply feeds different category filling areas;
- Interconnection of incompatible supply gases shall not be possible through the various cylinder filling manifolds and mixing systems. Non-return valves and block valves shall not be relied on as the only means of protection against interconnection of incompatible gases;
- Connections to the cylinder filling manifold system shall be designed to avoid the possibility of connection of unauthorised products. (i.e., exclusion of oxidants from cylinder filling manifolds to be used exclusively for flammable gases);
- Temperature sensitive components (e.g., polymer gaskets) should be avoided where there is a risk of high temperatures occurring. The systems should be designed to avoid the risks associated with adiabatic compression of gases;
- Pressure sensing devices and other cylinder filling manifold equipment shall be selected to ensure that they give meaningful indications to the operator and are pressure rated for the system. It may be desirable to fit over-pressure protecting devices to low pressure sensing devices that are incorporated in high pressure systems. However, such devices might not always work, so it is advisable to also fit gauge isolating valves;

- Provision should be made for “parking” positions for cylinder filling hoses, so that dirt and atmospheric contamination is excluded when the hoses are not in use;

- There should be adequate labelling to identify valves and other operating controls and equipment; and

- The number and size of cylinders permitted to be filled on the system should be defined and easily accessible to the operator. For automated gravimetric fill systems both the pressure and mass measurements are vital to ensure that the cylinders cannot be overfilled if wrong cylinder is connected.

7.2.5 Operation of gas mixture filling facilities

In addition to the provision of equipment operating instructions and gas mixture filling instructions (recipes), the following safeguards shall be in place:

- Checks to be made by the fill operator to ensure that the cylinder and valve are in good condition and within the re-inspection period;

- Checks to be made by the fill operator to verify the pressure rating of the cylinder and where appropriate perform a tare check of the cylinder to verify cylinder is empty;

- There shall be adequate segregation of cylinder supply gases (i.e., pure products and premixes);

- Pure products and premixes shall be clearly identified with all relevant markings and current composition information of the contents in the appropriate language for the operator;

- Piped gas supply lines shall be adequately purged prior to use to avoid incompatible reactions and potential contamination issues;

- Cylinder valve outlet adapters should be controlled in line with the level of risk in the event of their incorrect or mistaken use. Adapters that enable inter-connection of incompatible gases should not be readily available in the gas mixing area – such adapters should be closely controlled (e.g., kept in a secure place and only issued for specific purposes);

- Where gas mixtures are prepared by non-dynamic methods, provision shall be made for homogenising these gas mixtures during or after filling where this is required by the mixing instructions. Cylinder rolling and/or the fitting of dip tubes within cylinders are mixing methods commonly employed. The design of the rolling machine shall ensure that loosening of the cylinder protective cap will be minimized. In particular, the use of flat or horizontal rolling machines is only recommended with additional safeguards, e.g., control of rolling direction; and

- Analysis of the intermediate mixture can be used to verify the composition of the mixture prior to adding the incompatible components.

7.2.6 Gas analysis

The following brief notes are given for guidance:

- Gas analysis facilities should be provided to fulfil the following functions:

    - Identify and verify the quality of the gas mixture components

    - Verify the composition of the final gas mixture and any intermediate mixtures as required by the gas mixing instructions

    - Identify the composition of gases and gas mixtures in returned cylinders;

- Commonly available gas analysis equipment of the type that is required to analyse the multiplicity of gas mixtures and their trace impurities is not normally of certified flameproof construction and often does not lend itself to inert gas purging. This shall be recognised when specifying the siting of equipment, its environment and the construction of sampling systems. However, this is not required for installations in non-classified areas (see 7.1 and 7.2.4 for more information on hazardous area classification and requirements for potentially explosive atmospheres);

- It is recommended when analysing flammable and/or toxic gases and mixtures to provide environmental monitoring equipment and or to provide additional localised ventilation;

- Proper arrangements shall be made for the safe disposal of gas samples; and

- Where analysis equipment is used with incompatible gases purging facilities shall be installed for the sampling and analysis systems.

8 Personnel training

Personnel involved in the handling of cylinders and mixing of gases shall be trained to an appropriate level that is commensurate with their degree of involvement. A formal training programme shall be undertaken against all relevant written operating procedures, recorded, and regularly updated. Personnel who carry out safety-critical activities (e.g., the manufacture of flammable plus oxidant gas mixtures) shall undergo formal competence checks to ensure they have a complete understanding of the processes, topics, and other material on which they have been trained.

Competence checks shall be recorded and signed by both trainer and trainee. Also, for certain safety-critical activities it may be advisable to perform psychological screening checks and/or unscheduled personnel screening programmes for drugs, alcohol, etc. This section sets out some of the training topics for consideration.

8.1 All personnel

Regular training reviews should be conducted to review ongoing training needs of all personnel. In addition, all relevant personnel shall be made aware of the hazards of any new products and/or changes to operating procedures and systems. A policy shall be established to define the activities for which the understanding and competence of individuals shall be periodically re-assessed and with what frequency. Personnel meeting the requirements of the competence checks would then be authorised to perform the tasks against which they have been checked. In addition to specific job training, some of the following training topics shall be considered:

- site safety rules and company’s safety policy;

- emergency and site evacuation procedures;

- use of PPE;

- awareness of permit to work system;

- identification of cylinder contents;

- basic physical, chemical, and hazardous properties of gases handled;

- safe handling and storage of cylinders;

- different sizes, types etc. of cylinders; and

- different cylinder valve types, valve outlets and applications.

8.2 Cylinder reception personnel

In addition to 8.1 and specific job training, training topics to be considered should include the following:

- recognition of cylinders received in a potentially hazardous condition and the immediate action to be taken; and
- cylinder retest date requirements.

8.3 Gas disposal personnel

In addition to 8.1 and specific job training, training topics to be considered should include the following:

- Detailed understanding of the physical, chemical, and hazardous properties of the gases and disposal reagents being handled;
- Key safety rules including seeking expert advice on cylinders with unknown contents or of unknown origin or with inoperable valves. Ensuring cylinders are made safe and appropriately labelled before being sent to the cylinder maintenance workshop; and
- Safe and environmentally responsible disposal of waste gases and operation of waste gas disposal equipment (written procedures to be provided).

  See also AIGA 083 [4].

8.4 Cylinder maintenance personnel

In addition to 8.1 and specific job training, training topics to be considered should include the following:

- cylinder maintenance and test rules and regulations;
- understanding of different types of cylinders, their identification and markings and their applications;
- understanding of different types of cylinder valves and their applications;
- procedures for change of gas service for cylinders;
- safety rules for cylinder maintenance (such as ensuring cylinders are de-pressurised and freed from hazardous gases before valve removal);
- rejection criteria for unsuitable cylinders and rejection of cylinders of unknown origin;
- procedures to scrap unserviceable cylinders;
- cylinder painting requirements; and
- safe operation of cylinder maintenance plant (written procedures shall be provided).

8.5 Cylinder filling personnel

In addition to 8.1 and specific job training, training topics to be considered should include the following:

- Detailed understanding of the physical, chemical and hazardous properties of the gases and materials being handled;
- Personnel involved in the mixing of flammable plus oxidant or other potentially reactive mixtures should have previous experience in other gas mixture filling and receive additional training on the specialised requirements of producing these mixtures;

- Key safety rules; examples include:
    - No gases are to be mixed without written instructions
    - No cylinders are to be filled unless they are in good condition, correctly supplied, correctly labelled for their intended contents and within statutory the test period
    - Rejection of unsuitable cylinders, including cylinders of unknown origin;
- Operation of gas mixing equipment (written procedures shall be provided);
- Checks during and after cylinder filling (including correct cylinder, valve operation, leak checks, and fitting of valve outlet cap nuts or plugs where appropriate); and
- Safe disposal of waste gases and operation of waste gas disposal equipment (written procedures shall be provided).

8.6 Gas analysis personnel

In addition to 8.1 and specific job training, training topics to be considered should include the following:

- detailed understanding of the physical, chemical, and hazardous properties of gases and materials being handled;
- operation of gas analysis equipment (written procedures to be provided);
- awareness of product specifications; and
- checks during and after gas analysis including correct cylinder valve operations, correct connection between cylinder and gas analysis equipment, leak checks, and fitting valve outlet cap nuts or plugs where appropriate, fitting valve protection covers.

8.7 Cylinder shipping personnel

In addition to 8.1 and specific job training, training topics to be considered should include the following:

- ensuring that the cylinder valve is firmly closed, and the valve outlet plug or cap nut fitted where appropriate;
- ensuring that the valve protection cover is properly fitted; and
- ensuring that the cylinders are labelled according to regulations and internal procedures.

8.8 Plant maintenance personnel

In addition to 8.1 and specific job training, training topics to be considered should include the following:

- Understanding of physical, chemical, and hazardous properties of the gases and materials being handled;
- The company’s planned maintenance policy (where appropriate);
- Necessary skills in fitting, welding, and electrical, etc.;
- Provision of equipment drawings, maintenance procedures, etc.;
- Key safety rules. These include:

- Permit to work system (where applicable)
- Not to start maintenance work until the plant and area are declared to be safe by a competent person
- Labelling of equipment to ensure it remains safe whilst maintenance work is in progress
- Special personal protective measures; and

- Disposal arrangements for potentially contaminated waste materials (e.g., oils, solvents etc.).

8.9 Personnel engaged in preparing operating procedures and gas mixing instructions

Personnel who prepare and check operating procedures and gas mixing instructions shall be technically competent, experienced in the gas industry and able to prepare concise and easily understood written instructions. They shall have received training in their company's requirements with respect to the style of the gas mixing instructions they prepare. Personnel engaged in preparing gas mixing instructions, in addition to having practical experience of gas mixing operations, shall have a proven knowledge of and access to the information on the physical, chemical, and hazardous properties of the gases being handled. In particular, they shall have access to the latest revision of the SDS of the products. They shall also have the necessary mathematical and computer skills (where computers are used) to carry out the appropriate calculations. They should also communicate regularly with cylinder filling personnel. Additional training requirements include:

- good knowledge of applicable legislation;
- knowledge of the company system that authorises changes to equipment and procedures;
- assessment of material compatibility; and
- identification of potential hazards and material compatibility issues for products not previously handled.

8.10 Personnel engaged in plant and equipment design

Personnel who design plant and equipment shall be technically competent and fully understand the physical, chemical, and hazardous properties of the gases being handled. Such personnel will possess a recognised qualification in an appropriate engineering subject (e.g., chemical, mechanical or electrical engineering), or will be knowledgeable and experienced and qualified by the company. They shall have the necessary skills to carry out appropriate design calculations and check specifications of bought-in-plant and equipment (e.g., material compatibility, pressure ratings etc.). They shall have the necessary skills to ensure that the plant they design incorporates all the necessary safety features to ensure safe operation. Often, such personnel need to be able to oversee the installation and testing of plant and equipment to ensure the work is carried out to the required standards.

8.11 Other personnel

Certain personnel in direct contact with customers and gas users, such as sales and marketing staff may need a basic understanding of the specific safety requirements related to the mixing of gases to ensure they refer certain gas mixtures to technical personnel before a commitment is made to produce. It is also helpful if they have a basic understanding of the safe handling of cylinders to enable them to respond correctly to simple customer enquiries.

8.12 First-aid training

There shall be an adequate number of personnel trained to carry out first aid in the event of personal injury at work. Where toxic or corrosive gases are handled, access to specially trained first aid and medical personnel should be available. Such personnel shall be aware of the special properties of the

substances being handled, have the necessary first aid requisites readily available and be qualified to administer them.

9 Safety

All normal requirements for the safe handling, storage, filling and maintenance of cylinders and filling systems for pure gases (such as industrial gases) also apply to gas mixtures. This section identifies some of the issues for consideration.

9.1 Provision of personal protective equipment and tools

Protective equipment shall include those specified in the SDS of the products being handled. Additional equipment shall be specified by the risk assessment.

For information regarding the use of non-sparking tools, see CGA PS-55, *CGA Position Statement on Use of Nonsparking Tools* [16].

9.2 Safety rules

The fundamental safety rules that apply to the gas mixing facility shall be documented, form part of the employees' training requirements and shall be rigorously enforced. Safety rules are likely to include requirements for the following:

- Personnel training in the duties that they have to carry out;
- PPE;
- No smoking areas and areas where smoking materials and other potential ignition sources are forbidden. Consideration shall also be given to restricting the use of portable electrical appliances in such areas (e.g., mobile telephones);
- Permit to work system, particularly with respect to maintenance work in potentially hazardous areas; and
- Site emergency procedures including evacuation, individual's responsibilities and location and use of emergency equipment.

9.3 Emergency planning

There should be published emergency response plans that are regularly practised. These plans shall have a primary regard for the safety of personnel and should take account of response requirements out-of-normal working hours. Key points for consideration when formulating emergency response plans include the following:

- Legal requirements;
- Provision of alarm systems;
- Action lists and procedures for personnel in the event of an emergency (e.g., for safe emergency shut-down of equipment and processes);
- Plans for site evacuation, roll calls and search for unaccounted personnel and their possible rescue;
- Site emergency response team, including individual's responsibilities, means of communication and back-up;
- Provision of emergency equipment (this could include positive pressure breathing equipment, specialised protective clothing, firefighting equipment, first aid equipment, emergency

communication equipment, tools and other requisites for sealing leaking cylinders and valves, provision of a salvage pressure receptacle when necessary);

- Emergency power supplies (e.g., for emergency lighting);
- Consultation and communication with the public emergency services (e.g., fire brigade, ambulance, police, local hospital etc.);
- Evaluation of risks and procedures to deal with specific foreseeable scenarios, e.g., toxic gas release; liquid releases and how to avoid their entry into drains and water courses; cryogenic gas releases; oxidant-rich atmospheres; filling-hose fire; burst-disc rupture; oxygen ignitions; how to deal with suspect unstable cylinders, etc;
- Consultation and communication with neighbours;
- Communication with the media (who should do this and what training do they need);
- Provision, location, regular checks and appropriate personnel training in the use of emergency equipment (e.g., firefighting equipment, first aid requisites, breathing apparatus and special protective clothing);
- Provision of site plans showing the location of hazardous materials and emergency equipment;
- Provision of data on all products and cylinders and cylinder valves; and
- Procedure for advising personnel that areas are safe for re-entry and re-instatement of emergency equipment.

See also EIGA Doc 60, *Seveso Documents - Guidance on Applicability, Assessment and Legal Documents for Demonstrating Compliance of Industrial Gases Facilities with Seveso Directive(s)* [17].

9.4 Audits

Regular audits of the gas mixing facility should be carried out by a competent person who is familiar with the operational and safety requirements. Audit techniques vary, however, it is recommended that audits should be recorded, together with any action points, and should include the following (not an exhaustive list):

- Are written instructions provided? (see 4.1);
- Are change management procedures in place and being followed? (see Section 7);
- Are equipment and facilities properly designed and approved? (see 4.2);
- Are there adequate safeguards to prevent feed-back of gases into the supply systems? (see 4.2);
- Are waste gases being safely disposed? (see 4.2);
- Are written instructions prepared by competent personnel? (see 4.3);
- Are compatibility data available for the gas mixture components both with each other and with the cylinder valve? (see 4.3);
- Are margins of safety documented for formulating mixing instructions for potentially incompatible gases such as oxidants and flammables? (see 4.3);

- Is there a safety approval system in operation for gas mixing instructions for mixtures containing potentially incompatible components, toxic gases and highly reactive gases? (see 4.3);
- Are the controls on mixture adjustment understood? (see 6.6 & 6.7);
- Is there a programme of planned and recorded training in operation? (see 4.4);
- Are cylinders marked with their intended contents prior to filling? (see 4.5);
- Are there controls to ensure that only intended supply gases are used? (see 4.6);
- Are there controls to ensure that only suitable cylinders are used, which are properly prepared and free from contaminants? (see 4.6);
- Are all operations covered by written operating instructions and personnel training records kept up-to-date? (see 4.4);
- From a check on a representative sample of plant operating procedures, is it clear that procedures are being followed correctly? (see 4.1 & 7.2.5);
- Were employees interviewed familiar with the site safety rules and emergency procedures? (see 9.2 & 9.3);
- Is there a control procedure for modification to plant, equipment and procedures and is it being followed? (see Section 7);
- Is there a safe system for gas disposal and is it being followed and checked periodically? (see 7.2.2);
- Are there systems for prevention of feed-back of gases into cylinders and are they being checked periodically? (see 7.2.2);
- Is there evidence that plant maintenance is being carried out in accordance with company requirements? (see 8.8);
- Is there evidence that the permit to work system is operating correctly? (see 8.8);
- Is there evidence that safety and emergency equipment is regularly inspected and maintained and kept in the correct location? (see 9.3);
- Is there evidence that gas monitoring equipment is regularly checked and calibrated and in working order? (see 7.1);
- Can it be verified that safety checks are carried out on cylinders after filling and analysis (e.g., leak-tests, fitting of valve outlet cap-nuts or plugs for toxic gases etc.)? (see 8.6, 8.7);
- Are cylinders stored safely in the correct locations? (see 7.1); and
- During the audit, observation of operators should be made in order to record any unsafe practices or failure to wear and use PPE as required by company safety rules.

10 References

Unless otherwise specified, the latest edition shall apply.

[1] AIGA 058, *Safe Preparation of Compressed Oxidant-Fuel Gas Mixtures in Cylinders*, European Industrial Gases Association. www.asiaiga.org

NOTE—This publication is part of an international harmonisation programme for industry standards. The technical content of each regional document is identical, except for regional regulatory requirements. See the referenced document preface for a list of harmonised regional references.

[2] AIGA 023, *Good Manufacturing Practice Guide for Medicinal Gases*, European Industrial Gases Association. www.asiaiga.org

[3] ADR *European Agreement concerning the International Carriage of Dangerous Goods by Road*. www.unece.org

[4] AIGA 083, *Disposal of Gases*, European Industrial Gases Association. www.asiaiga.org

NOTE—This publication is part of an international harmonisation programme for industry standards. The technical content of each regional document is identical, except for regional regulatory requirements. See the referenced document preface for a list of harmonised regional references.

[5] ISO 11114-1, *Gas cylinders — Compatibility of cylinder and valve materials with gas contents — Part 1: Metallic materials*, International Standards Organization. www.iso.org

[6] ISO 11114-2, *Gas cylinders — Compatibility of cylinder and valve materials with gas contents — Part 2: Non-metallic materials*, International Standards Organization. www.iso.org

[7] AIGA 065, *Avoidance of Failure of Steel Cylinders Containing CO and CO/CO2 Mixtures*, European Industrial Gases Association. www.asiaiga.org

NOTE—This publication is part of an international harmonisation programme for industry standards. The technical content of each regional document is identical, except for regional regulatory requirements. See the referenced document preface for a list of harmonised regional references.

[8] EIGA Doc 100, *Hydrogen Cylinders and Transport Vessels*, European Industrial Gases Association. www.eiga.eu

[9] ISO 11621:1997, *Gas cylinders — Procedures for change of gas service*, International Standards Organization. www.iso.org

[10] CGA C-10, *Guideline to Prepare Cylinders and Tubes for Gas Service and Changes in Gas Service*, Compressed Gas Association, Inc. www.cganet.com

[11] TRGS 407, Tätigkeiten mit Gasen – Gefährdungsbeurteilung. https://www.baua.de/

[12] NOAA Expanded Chemical Reactivity Worksheet (CRW4)

[13] Regulation (EC) No. 1272/2008 of the European Parliament and of the Council on classification, labelling and packaging of substances and mixtures. https://eur-lex.europa.eu/

[14] Directive 2014/34/EU concerning equipment and protective systems intended for use in potentially explosive atmospheres, European Commission. www.ec.europa.eu

[15] Directive 1999/92/EC on minimum requirements for improving the safety and health protection of workers potentially at risk from explosive atmospheres (ATEX), European Commission. www.ec.europa.eu

[16] CGA PS-55, *CGA Position Statement on Use of Nonsparking Tools*, Compressed Gas Association, Inc. www.cganet.com

[17] EIGA Doc 60, *Seveso Documents - Guidance on Applicability, Assessment and Legal Documents for Demonstrating Compliance of Industrial Gases Facilities with Seveso Directive(s)*, European Industrial Gases Association. www.eiga.eu

[18] R. C. Reid, J. M. Prausnitz, B. E. Poling: “The Properties of Gases and Liquids”, 4th edition., McGraw-Hill, 1987. www.mcgraw-hill.com

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ISO 10156, *Gases and gas mixtures - Determination of fire potential and oxidizing ability for the selection of cylinder valve outlets*, International Standards Organization. www.iso.org

ISO 6142-1, *Gas analysis -- Preparation of calibration gas mixtures -- Gravimetric methods*, International Standards Organization. www.iso.org

ISO 6144, *Gas analysis -- Preparation of calibration gas mixtures -- Static volumetric method*, International Standards Organization. www.iso.org

ISO 6145-1, *Gas analysis -- Preparation of calibration gas mixtures using dynamic volumetric methods -- Part 1: Methods of calibration*, International Standards Organization. www.iso.org

ISO 6145-2, *Gas analysis -- Preparation of calibration gas mixtures using dynamic methods -- Part 2: Piston pumps*, International Standards Organization. www.iso.org

ISO 6145-4, *Gas analysis -- Preparation of calibration gas mixtures using dynamic volumetric methods -- Part 4: Continuous syringe injection method*, International Standards Organization. www.iso.org

ISO 6145-5, *Gas analysis -- Preparation of calibration gas mixtures using dynamic volumetric methods -- Part 5: Capillary calibration devices*, International Standards Organization. www.iso.org

ISO 6145-6, *Gas analysis -- Preparation of calibration gas mixtures using dynamic methods -- Part 6: Critical flow orifices*, International Standards Organization. www.iso.org

ISO 6145-7, *Gas analysis -- Preparation of calibration gas mixtures using dynamic methods -- Part 7: Thermal mass-flow controllers*, International Standards Organization. www.iso.org

ISO 6145-8, *Gas analysis -- Preparation of calibration gas mixtures using dynamic volumetric methods -- Part 8: Diffusion method*, International Standards Organization. www.iso.org

ISO 6145-9, *Gas analysis -- Preparation of calibration gas mixtures using dynamic volumetric methods -- Part 9: Saturation method*, International Standards Organization. www.iso.org

ISO 6145-10, *Gas analysis -- Preparation of calibration gas mixtures using dynamic volumetric methods -- Part 10: Permeation method*, International Standards Organization. www.iso.org

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Appendix A – List of unstable gases (Informative)

Usual name	Chemical formula	CAS Registry Number
Acetylene[1)]	C2H2	74-86-2
Bromotrifluoroethylene	C2BrF3	598-73-2
Butadiene-1,2	C4H6	590-19-2
Butadiene-1,3	C4H6	106-99-0
Ethyl acetylene	C4H6	107-00-6
Cyanogen Chloride	ClCN	506-77-4
Chlorotrifluoroethylene	C2ClF3	79-38-9
Hydrogen cyanide	HCN	74-90-8
Diborane [1)]	B2H6	19287-45-7
Cyanogen	C2N2	460-19-5
1,1-Difluoro ethylene	C2H2F2	75-38-7
Ethylene	C2H4	74-85-1
Ethylene oxide[1)]	C2H4O	75-21-8
Hydrogen iodide	HI	10034-85-2
Methyl nitrite[1)]	CH3NO2	624-91-9
Methyl vinyl ether	C3H6O	107-25-5
Propadiene	C3H4	463-49-0
Propylene	C3H6	74-99-7
Stibine[1)]	SbH3	7803-52-3
Tetrafluoroethylene	F2C=CF2	116-14-3
Tetrafluorohydrazine	N2F4	10036-47-2
Vinyl bromide	C2H3Br	593-60-2
Vinyl chloride	C2H3Cl	75-01-4
Vinyl fluoride	C2H3F	75-02-5

NOTE—ΔGf, free enthalpy of formation from R. C. Reid, J. M. Prausnitz, B. E. Poling: "The Properties of Gases and Liquids", 4th edition, McGraw-Hill, 1987 [15].

1) Unstable at standard conditions.

The following oxidant gases are known to decompose at elevated temperature or pressure.

Usual name	Chemical formula	CAS Registry Number
Nitric oxide	NO	10102-43-9
Nitrous oxide [1)]	N_2O	10204-97-2
Ozone	O_3	10028-15-6

NOTE—ΔG_f, free enthalpy of formation from R. C. Reid, J. M. Prausnitz, B. E. Poling: "The Properties of Gases and Liquids", 4th edition, McGraw-Hill, 1987 [18].

1) At temperatures over 575°C [1013°F] and at atmospheric pressure, nitrous oxide decomposes into nitrogen and oxygen.