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Guidelines on characterization and testing of membranes for gas separation applications

Lignes directrices sur la caractérisation et
l'essai des membranes pour les applications
de séparation des gaz

Leitlinien zur charakterisierung und
prüfung von membranen für
gastreanwendungen

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Contents	Page
Foreword.....	4
Introduction	6
1 Scope.....	7
2 Normative references.....	8
3 Terms and definitions	8
4 Membrane material classification	12
4.1 General.....	12
4.2 Polymeric membranes.....	12
4.2.1 General.....	12
4.2.2 Membranes made of glassy polymers	13
4.2.3 Membranes made of rubbery polymers	13
4.2.4 Membranes made of blockcopolymers	13
4.3 Inorganic membranes	13
4.3.1 General.....	13
4.3.2 Ceramic membranes.....	13
4.3.3 Metallic membranes	13
4.3.4 Carbon membranes.....	13
4.4 Membranes employing material combinations.....	13
4.4.1 Mixed matrix membranes.....	13
4.4.2 Facilitated transport membranes.....	14
4.4.3 Supported liquid membranes	14
5 Membrane geometry classification.....	14
5.1 General.....	14
5.2 Flat sheet membranes.....	14
5.3 Tubular membranes	14
6 Membrane morphology classification.....	14
6.1 Homogenous membranes	14
6.2 Asymmetric membranes	14
6.2.1 General.....	14
6.2.2 Integrally skinned asymmetric membranes.....	15
6.2.3 Composite membranes	15
7 Single gas permeation	15
7.1 General.....	15
7.2 List of gases	15
7.3 Constant volume-variable pressure methods (CVVPM)	16
7.3.1 General.....	16
7.3.2 Time-Lag method	17
7.3.3 Pressure increase method.....	18
7.3.4 Flash evaporation of vapours	18
7.4 Variable flow, constant pressure method.....	18
8 Mixed gas permeation	20
8.1 General.....	20
8.2 List of gas mixtures	20

8.3	Constant volume-variable pressure method (CVVPM)	21
8.4	Variable flow, fixed pressure method	21
8.4.1	General	21
8.4.2	Controlled evaporation	22
8.4.3	Saturation methods	22
8.5	Guidelines to ensure measurements of intrinsic membrane properties.....	22
8.5.1	Membrane pretreatment to remove any remainders of membrane preparation history..	22
8.5.2	Testing repetition under the same conditions with either the same membrane sample or different membrane samples obtained in the same membrane preparation conditions..	23
8.5.3	Testing of membrane stability and potential aging	23
8.6	Guidelines for composition analysis.....	23
9	Reporting and models.....	23
9.1	Reporting.....	23
9.2	Recommended models	24
	Bibliography	25

Foreword

This CEN Workshop Agreement (CWA 18200:2025) has been developed in accordance with the CEN-CENELEC Guide 29 “CEN/CENELEC Workshop Agreements – A rapid way to standardization” and with the relevant provisions of CEN/CENELEC Internal Regulations - Part 2. It was approved by the Workshop CEN “Characterization and testing of membranes for gas separation applications”, the secretariat of which is held by the Spanish Association for Standardization, UNE, consisting of representatives of interested parties on 2024-10-30, the constitution of which was supported by CEN following the public call for participation made on 2024-05-31. However, this CEN Workshop Agreement does not necessarily include all relevant stakeholders.

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Introduction

The CEN Workshop Agreement Characterization and testing of membranes for gas separation applications addresses the fact that membrane technology has become a viable technology for various separation tasks in numerous industries, energy generation, environmental protection, wastewater treatment and clean water provision, to name but a few. Both liquid and gas phase mixtures are being treated. Furthermore, membranes can be classified according to the materials or material combinations they are made from as well as their geometrical form. Gas phase separation has gained in importance in the recent years, especially when considering the separation needs arising from the transition of Europe's industry towards CO₂-neutrality and zero discharge operation. Membrane technology can play a very important role here since it exhibits numerous advantages when compared to other separation technologies as e.g. ease of scalability and operation, steady state operation, small footprint area, energy efficiency and avoidance of potentially harmful chemicals during operation, to name but a few. However, the methods and protocols employed by manufactures, industrial users and academia to assess and classify the separation properties of individual membranes differ widely. To realise the potential of gas separation membrane technology it is necessary to be able to select the right membrane for the given separation task. This entails a true comparability of reported performance and operating window data for membranes based on thorough testing. The main objective of this document is to provide a detailed set of common procedures, methodologies and protocols to be applied when determining characteristics of gas separation membranes that will allow for comparable and homogeneous results independent of the details of the instrumental infrastructure at the individual institutions.

1 Scope

This document deals with membranes employed for the separation of gas streams. Membranes such as those employed in fuel cells are explicitly not in the scope of the document. Its aim is to derive a common understanding that will allow for a fair comparison between different gas separation membranes used for various separation tasks. It defines a detailed set of common procedures to determine the specific characteristics of the membranes under different operating conditions.

In particular, the following points are addressed:

- General aspects:
 - o Definition of materials used for membrane manufacture and membrane
 - o Classification of membrane:
 - Material of the selective layer
 - Material of the support
 - Type as e.g. mixed matrix membrane
 - Geometry
 - o Experimental accuracies/errors
 - o Assessment of aging
 - o Account for real gas behaviour
- Equipment design:
 - o Temperature, pressure and flowrate measurement devices and procedures
 - o Dimensioning of pipework with respect to pressure drops
- Single gas permeation performance:
 - o How to assess the permeation of vapours
 - o Temperature and pressure ranges
 - o Used methods for permeation measurements
 - o Compare membranes made of different materials: definition of parameters for comparison, e.g. selectivity and permeance
- Gas mixtures:
 - o Definition of representative applications for membrane gas separations. This includes the definition of gas mixtures
 - o Definition of operating conditions: temperatures, pressures, compositions, use of sweep gas
 - o Consideration on the intrinsic membrane performance assessment, avoiding influence of:

- Concentration polarisation
- Change of composition along the membrane surface
- o Composition analysis recommendations regarding applicable instruments and methods
- Reporting the results:
 - o Recommended extent of data to be reported, including that on experimental procedure.

The resulting CWA will be applicable to manufactures of gas separation membranes in academia and industry. The results will form a valuable basis for design for chemical manufacturing companies as well as E&C companies. It will allow these companies to consider membrane gas separation in the early design phases and hence allow to develop more environmentally friendly, energy efficient and low carbon footprint processes.

2 Normative references

There are no normative references in this document.

3 Terms and definitions

For the purposes of this document, the following terms and definitions apply.¹

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

- ISO Online browsing platform: available at <http://www.iso.org/obp/>
- IEC Electropedia: available at <http://www.electropedia.org/>

3.1

porous membrane:

membrane containing pores (voids)

[SOURCE: ISO 20480-3:2021]

3.2

asymmetric membrane

membrane constituted of two or more structural planes of nonidentical morphologies

3.3

composite membrane

membrane having chemically or structurally distinct layers

3.4

dense non-porous membrane

membrane with no detectable pores

¹ The terms and definition from 3.2 up to and including 3.24 are relevant for gas separation and have been given in Reference [2].

3.5**flux**

number of moles, volume, or mass of a specified component i passing per unit time through a unit of membrane surface area normal to the thickness direction

3.6**fouling**

process resulting in loss of performance of a membrane due to the deposition of suspended or dissolved substances on its external surfaces, at its pore openings, or within its pores

3.7**homogenous membrane**

membrane with essentially the same structural and transport properties throughout its thickness

3.8**ideal separation factor**

parameter defined as the ratio of the permeability coefficient of component A to that of component B and equal to the “separation factor” where a perfect vacuum exists at the downstream membrane face for gas and vapor permeation systems

3.9**membrane**

structure, having lateral dimensions much greater than its thickness, through which mass transfer may occur under a variety of driving forces

3.10**membrane compaction**

compression of membrane structure due to a pressure difference across its thickness

3.11**membrane conditioning, pretreatment**

process carried out on a membrane after the completion of its preparation and prior to its use in a separation application

Note 1 to entry: Thermal annealing to relieve stresses or pre-equilibration in a solution similar to the feed stream it will contact are examples of conditioning treatments.

Note 2 to entry: Conditioning treatments differ from post-treatments, since the latter occur before exposure to feed type solutions, while conditioning may occur using actual feed solutions.

3.12**membrane physical aging**

change in the transport properties of a membrane over a period of time due to physical chemical structural alterations

3.13**membrane post treatment**

process carried out on a membrane after its essential structure has been formed but prior to its exposure to an actual feed stream

3.14**penetrant**

entity from a phase in contact with one of the membrane surfaces that passes through the membrane

3.15

permeability coefficient or permeability

parameter defined as a transport flux per unit transmembrane driving force per unit membrane thickness

3.16

permeance

transport flux per unit transmembrane driving force

3.17

permeant

3.18

permeate

stream containing penetrants that leaves a membrane module

3.19

retentate

stream that has been depleted of penetrants that leaves the membrane modules without passing through the membrane to the downstream

3.20

selective membrane skin

region, often located at the upstream face of an asymmetric membrane, that forms a thin, distinguishable layer primarily responsible for determining the permeability of the asymmetric membrane

3.21

separation factor

ratio of the compositions of components A and B in the permeate relative to the composition ratio of these components in the retentate

3.22

solution-diffusion

molecular-scale process in which penetrant is sorbed into the upstream membrane face from the external phase, moves by molecular diffusion in the membrane to the downstream face and leaves into the external gas, vapor or liquid phase in contact with the membrane

3.23

stage cut

parameter defined as the fractional amount of the total feed entering a membrane module that passes through the membrane as permeate

3.24

sweep

nonpermeating stream directed past the downstream membrane face to reduce downstream permeant concentration

3.25

concentration polarization

concentration boundary layer that is formed when a mixture of gases is passed over a membrane parallel to its surface and one or more components are more readily permeating than others.

Note 1 to entry: This results in a concentration gradients: the concentrations of the preferentially permeating components are lower at the membrane surface than in the bulk whilst it is vice versa for the retained components.

3.26**contrapermeation**

passage of components from the permeate side (i.e. the sweep gas) to the retentate or feed side

3.27**facilitated transport membrane**

membrane where the selective layer contains either fixed or mobile chemical groups (carriers) that reversely react with permeating components

Note 1 to entry: A mobile carrier will permeate towards the permeate side of the membrane where the bound permeating component is released and the carrier is permeating back to the feed side of the membrane. A fixed site carrier will pass the permeating component from carrier to carrier towards the permeate side. Hence, a permeance higher than achievable by the solution-diffusion mechanism can be achieved.

3.28**gutter layer**

first layer of typically low selectivity and high permeance coated onto the porous support of a thin film composite membrane, the purpose of which is to provide a smooth, defect-free surface for subsequent coating of selective layers as well as to provide ready access for the porous support structure, also by allowing for diffusion of permeating components in parallel to the membrane surface

Note 1 to entry: This implies that the material is highly permeable compared to the selective layer and that it is compatible to the selective layer.

3.29**mixed matrix membrane (MMM)**

membrane, selective layer of which consists of more than one material type and hence possesses a continuous, typically polymeric, and a dispersed phase

Note 1 to entry: The latter can be comprised of finely dispersed inorganic particles. These particles can aid membrane stability and in this functionality be used in both support and selective layers or possess a separation functionality when employed in the separation layer.

3.30**non-woven**

typically polymeric, flat sheet material characterized by a smooth surface onto which a porous support layer can be cast

Note 1 to entry: Furthermore, a non-woven is characterized by its high porosity and permeance. Hence, it should pose only a minimal resistance to mass transfer and its impact will not be considered.

3.31**plasticization**

depending on the polymer the reversible or the non-reversible change in the state of the membrane polymeric material, e.g. porosity and free-volume, due to the interaction, typically at high pressure, with gases such as carbon dioxide

3.32**protection layer**

last layer coated on top of the actual separation layer to plug any pinholes and provide protection

Note 1 to entry: The protection layer is typically made of a, compared to selective layer, highly permeable material. It can be applied to thin film composite as well as integrally skinned asymmetric membranes.

3.33

selective layer

layer of a membrane where the separation occurs

Note 1 to entry: This is typically a dense layer for polymer and metal membranes and a porous layer for different types of ceramic or carbon membranes.

3.34

support layer

porous structure that supports the typically thin gutter or separation layers, and which can consist of a symmetric or asymmetric pore structure depending on the material it is manufactured from and the process employed to manufacture the support layer

Note 1 to entry: Typical requirements are a good compatibility to subsequent layers when employed as part of a composite membrane and a low resistance to mass transfer as well as a low pressure drop. Whilst it is understood that both pressure drop and resistance to mass transfer can be of importance, these phenomena will not be considered. The effects can be assumed to be of no influence as long as the permeance of the porous layer is at least ten times greater than that of the separation layer. Especially in the case of high flux thin film composite membranes careful testing should be conducted to assess whether there is an influence of transport in the support layer on the reported result.

3.35

swelling

change of a polymer separation layer caused by the solution of permeating components into the polymer, which typically results in a change of separation characteristics of the polymer separation layer

Note 1 to entry: This typically is a reversible effect.

3.36

thin film composite membrane (TFCM)

type of composite membrane where the thickness of the separation layer is minimized

Note 1 to entry: A special case of TFCM is a thin film nanocomposite membrane (TFN), where the separation layer is of the mixed matrix type.

3.37

top healing layer

top layer of a highly permeable but not especially selective polymer to plug any pinholes and similar defects occurring during membrane production

4 Membrane material classification

4.1 General

Membranes can be manufactured from a multitude of different materials and combinations thereof. This section will describe the types.

4.2 Polymeric membranes

4.2.1 General

This section deals with membranes that are made of polymers only. By definition, these are dense, non-porous membranes since a selective permeation through these materials is only possible by means of the solution-diffusion mechanism.

4.2.2 Membranes made of glassy polymers

Glassy polymers are those that are below the polymer's glass transition temperature when employed as a membrane material. It is important to understand that this temperature might change due to the presence of the constituents of the gas mixture to be separated.

4.2.3 Membranes made of rubbery polymers

Rubbery polymers are those that are above the polymer's glass transition temperature when employed as a membrane material. It is important to understand that this temperature might change due to the presence of the constituents of the gas mixture to be separated.

4.2.4 Membranes made of blockcopolymers

Blockcopolymers are polymers that consist of more than one polymer block where the monomers are grouped in alternating blocks. They can consist of hard and soft segments, where the soft segments typically possess the permeation properties and the hard segments serve to provide the structural integrity.

Typical examples of these membrane blockcopolymers are commercial ones like Pebax or PolyActive, with rigid polyamide or polybutyleneterephthalate and soft and polar polyether groups, showing an elastomeric character.

4.3 Inorganic membranes

4.3.1 General

Inorganic membranes are typically consisting of a coarse, porous support and active layer on top of the support where the separation takes place applied. Inorganic membranes can be divided into the following membrane types.

4.3.2 Ceramic membranes

Gas-separating ceramic membranes mostly consist of metal oxides such as SiO_2 , Al_2O_3 , ZrO_2 , TiO_2 etc. and mixtures of these and, less frequently, of non-oxide materials such as SiC and Si_3N_4 . In the case of porous membranes, the pores are determined by the material structure in the order of a few nanometers, whereby irregular pores can exist in amorphous structures as well as regular pores in crystalline materials (e.g. zeolites). In non-porous ceramic materials, selective mass transport can also occur through ion hopping processes via defects, whereby a crystalline, non-stoichiometric structure is a prerequisite.

4.3.3 Metallic membranes

These are membranes that consist of a dense metal or metal alloy film, typically on a porous support structure not necessarily made of metal.

4.3.4 Carbon membranes

The separation layer here consists of carbon exhibiting a molecular sieve functionality. This layer typically is produced by pyrolyzing a polymer layer.

4.4 Membranes employing material combinations

4.4.1 Mixed matrix membranes

This is a membrane that typically consists of a polymer as a homogenous phase into which a typically inorganic material (such as silicas and zeolites and carbon-based ones, not excluding others like MOF-metal-organic frameworks, COF-covalent-organic frameworks, etc.) is dispersed as filler. The latter might influence the stability properties of the membrane with respect to swelling, membrane physical aging

and compaction or actively influence the transport properties by offering additional, selective functionality.

4.4.2 Facilitated transport membranes

This membrane type consists of a polymer matrix that in turn contains chemically reactive groups (such as an amine or organometallic complex, etc.). These can either reside at fixed locations (fixed site facilitated transport membranes) or move inside the membrane (mobile carrier). The chemically reactive group binds the permeating components and either passes it through the membrane from fixed site to fixed site along a concentration gradient whereas a mobile carrier reacts on the feed side with permeating component, moves through the membrane to the permeate side where the permeating component is released and the carrier moves through the membrane in the opposite direction.

4.4.3 Supported liquid membranes

This type of membrane consists of a liquid (such as an ionic liquid, etc.) that possesses preferential transport properties for one or more components to be separated. The liquid is immobilised in the porous structure of a support membrane.

5 Membrane geometry classification

5.1 General

Membranes can be manufactured as flat sheet material (to conform plate-frame and spiral wound modules) or in tubular form (to conform multitubular modules including hollow fiber membrane modules).

5.2 Flat sheet membranes

Flat sheet membranes have a planar geometry. They can be homogenous as well as asymmetric. These membranes can be produced on top of a non-woven as well as on a smooth surface as glass or polished stainless steel.

5.3 Tubular membranes

For gas separation these are on the one side polymeric membranes, typically of an asymmetric nature that are produced by a hollow fibre spinning process. Tubular geometries are typically used for inorganic membranes.

6 Membrane morphology classification

6.1 Homogenous membranes

These are membranes according to the definition of Clause 3. The cross section of the membrane is made of one material and homogenous, i.e. the transport properties are not varying between the feed/retentate and permeate side interface of the membrane.

6.2 Asymmetric membranes

6.2.1 General

This type of membranes can be sub-divided into two further types.

6.2.2 Integrally skinned asymmetric membranes

The membrane structure of an integrally skinned asymmetric membrane consists of one and the same material. For polymer membranes this is a function of the production process where a porous support structure densifies to form a dense, thin layer at the top.

6.2.3 Composite membranes

This type of membrane consists of more than one layer where the individual layers are produced in different production steps. They can, but do not have to, consist of different materials.

These can be in turn thin film composite (TFC) membranes, with dense skin layer controlling the membrane transport and providing the separation selectivity, and thin film nanocomposite (TFN) membranes, where the previous TFC membrane can be a MMM incorporating suitable filler nanoparticles.

7 Single gas permeation

7.1 General

The first step of assessing the applicability of a membrane for a specific separation task is to define its permeation properties for individual components. There are two main methods: the constant volume-variable pressure method (CVVPM) and the constant pressure method (CPM). In principle, both methods could be used for characterization of any membrane sample. However, CVVPM is generally used for samples with very low permeation rates, which are impossible to sense/measure precisely and accurately enough by any flowrate measurement device. An example are symmetric dense films. However, the method can also be applied to asymmetric membranes with high permeation rates, provided the instrumentation allows for a sufficient time resolution. On the other hand, CPM is used for membrane samples with higher gas permeation rates that are possible to be measured accurately by flow rate measurement devices. Membrane samples with asymmetric morphology are mostly investigated by the latter case method.

The single gas permeation performance described in this clause relates to the entire membrane. In case of asymmetric membranes as described in subclause 6.2. this means the measured value entails not only the performance of the actual separation layer but also those of possible non-woven supports, porous support layers as well as gutter and protection layers.

7.2 List of gases

In order to characterise the gas separation membranes, the (at least two of the) following gases should be employed to ensure a comparability.

1. Oxygen
2. Nitrogen
3. Carbon dioxide
4. Helium
5. Sulfurhexafluoride
6. Perfluoromethane
7. Xenon

If of interest and infrastructure (explosion-protection) allows:

8. Hydrogen
9. Methane
10. Ethane
11. Propane

Other gases can of course be included into the measurement programme, if of interest.

7.3 Constant volume-variable pressure methods (CVVPM)

7.3.1 General

Constant volume, variable pressure methods for gas permeation measurement involve two fixed volumes on both sides of a test cell containing the membrane or on fixed pressure and one fixed volume on either side of the test cell. The test cell has one gas inlet on the feed side and one gas outlet on the permeate side. The apparatus is tightly temperature controlled. The whole system is evacuated and the volume on the feed side is filled with one gas until a defined pressure is reached. At the start of the measurement, the feed volume is connected with the test cell and gas starts to permeate through the membrane. This causes the pressure in the feed volume to decrease and the pressure in the permeate volume to increase. The volumetric permeate flux at standard temperature and pressure can be calculated by the ideal gas law and a material balance around the permeate volume since the temperature, collection (permeate side) volume and the pressure change versus time (dp/dt) are known. In case the ideal gas law is not valid in the investigated temperature and pressure range, an appropriate equation of state has to be applied to account for the real gas behaviour. This information is used to calculate permeability or permeance. Two ways of operating these units are possible: time lag and pressure increase.

A simple schematic system for a CVVPM is shown below. More detailed design information could be found in the literature references [3-8]. The evaluation procedures are discussed in detail in these documents.

A generic procedure could be:

- degassing the membrane sample by pulling vacuum on both sides of the cell/module for a long enough period of time, e.g. degassing of the film is performed for at least 24 h or until a sufficient leak rate is obtained ($\sim 133,32 \times 10^{-6} \text{ Pa/s} = 1 \times 10^{-6} \text{ torr/s}$ or lower),
- closing all valves and performing a leak test by recording the pressure increase dp/dt ,
- pressurizing the upstream of the cell/module and starting the pressure recording on the permeate side versus time,
- when the pressure on the permeate side reaches to the limit of the pressure sensor or a pre-selected pressure value, stop recording the pressure, pull vacuum on the permeate side and restart recording the pressure. This procedure is repeated until the process reaches to the steady state.

This is a quite generic procedure to conduct a gas permeation measurement by a CVVP method. It is widely accepted approach that the slope value (dp/dt) should be at least two orders of magnitude larger than the leak rate.

The main concerns and advice for the designers and operators of such systems are;

- using stainless steel tubing,
- using larger size of tubing (minimum 6 mm or $\frac{1}{4}$ "),
- reducing the number of connections to reduce the leak rate,

- avoiding complex plumbing geometry for the downstream/permeate side volume. In other words; target less bending of tubing, tees and branches,
- do not locate the pressure transducer at the very far end of the permeate side volume,
- using gasket face seal fittings for the parts of the system that is under vacuum, i.e. those types of fittings specifically designed for vacuum usage,
- preferably use vacuum pumps of an operating principle that does not require oil in the gas compressing parts,
- apply solutions to prevent contamination by the vacuum pump in case of using oil containing vacuum pumps,
- make the upstream volume large enough to minimize the fluctuations in the feed pressure; i.e. adding a ballast volume, use automatic pressure controllers if possible,
- using gas independent pressure sensors with high accuracy and narrower possible range,
- locating all downstream volume within the temperature controlled environment or supply temperature control.

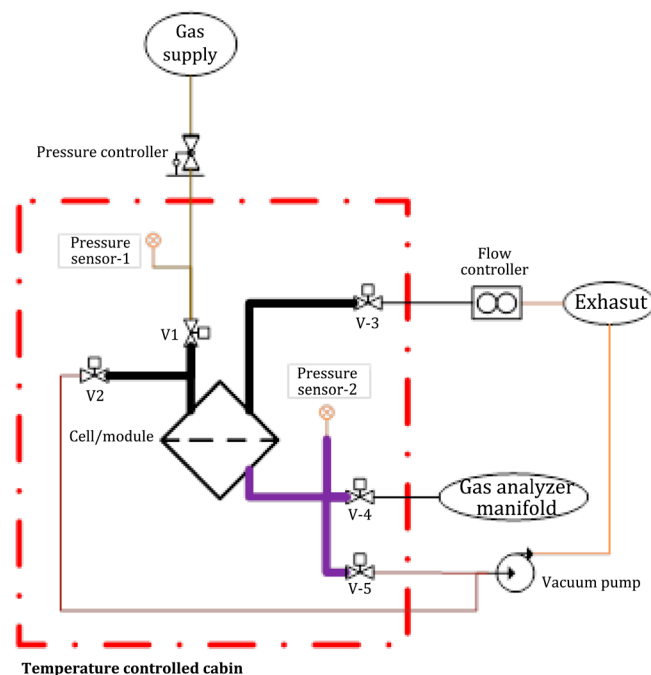


Figure 1 — General design of a constant volume, variable pressure device

7.3.2 Time-Lag method

For the time lag, the resolution of the pressure increase curve on the permeate side is that fine that delay of the pressure increase in the permeate volume is resolved and can be employed to determine the diffusion coefficient. The linear slope of the pressure in the permeate volume vs. time curve allows for the determination of the permeability in combination with the thickness. Solubility is then obtained as the ratio between permeability and diffusivity. In order for the time lag methods to work, the investigated,

typically homogenous membrane materials should have a thickness that allows for allow enough transmembrane flux for time resolution and easy handling. Recommended parameters are:

1. Temperature range selectable between -20°C and 900°C , the latter allowing for the investigation of ion-conducting membranes. At least four temperatures should be investigated when temperature dependency is to be reported. An individual temperature has to adjusted within $\pm 0,5\text{ K}$ of the reported value.
2. Pressure ranges can be selected freely for permanent gases as long as the assumption of ideal gas behaviour is valid. This can be verified using an appropriate equation of state or tabulated data. For condensable gases, typically ambient pressures and below are selected and the real gas behaviour should be accounted for.
3. Repetitions of experiments should be conducted to allow for statistically relevant results.
4. Membrane thickness measurement should be determined with high accuracy by measuring multiple points on the membrane surface and calculating the mean value.
5. Membrane area measurement should be conducted with care to account for O-ring geometry change due to compression and thermal expansion.
6. Permeation test duration: Permeation experiment should be prolonged for at least three times the time lag to ensure that the permeation process reaches the steady state.

The evaluation and additional theoretical background are supplied by Crank and Park [9] as well as Mears [10].

7.3.3 Pressure increase method

The pressure increase method essentially operates as described for the time lag method, only that typically asymmetric membranes are being investigated. This has the consequence, that the time lag due diffusion cannot be resolved and only the permeance can be determined. Recommended parameters are:

1. Temperature range selectable between -20°C and 450°C . At least four temperatures should be investigated when temperature dependency is to be reported. An individual temperature has to adjusted within $\pm 0,5\text{ K}$ of the reported value.
2. Pressure ranges should be selected as pointed out in subclause 7.3.2.
3. Repetitions. For permanent the resulting mean value should be statistically relevant. For condensable gases and vapours the number of points should give a clear picture of the permeance dependence on feed and permeate pressures.

7.3.4 Flash evaporation of vapours

The permeation of vapours can be measured by including a liquid reservoir isolated by a valve into the setup. The reservoir has to be placed into the temperature controlled section of the apparatus. Subjecting the reservoir to the pre-selected feed side pressure will cause the feed side to be filled with vapour according to the vapour pressure of the liquid. This entails the feed side pressure to be lower than ambient and accurate pressure measurement. Furthermore, only liquids with low boiling points are suitable. Examples are light hydrocarbons and alcohols as well as water.

7.4 Variable flow, constant pressure method

The method could simply be described as measuring the permeate flux under a constant transmembrane pressure. The volumetric permeate flux at standard temperature and pressure could be calculated by

ideal gas law or an appropriate equation of state since the temperature, the volumetric permeate flux and the pressure are known. This information is used to calculate permeability or permance.

Pressure is applied to the feed side and the permeate flux is measured by a flowmeter. Measurement is performed until the process reaching a steady state.

A simple schematic system for a CPM is shown below. More detailed design information could be found in the literature [11].

The main concern for the designers and operators of such systems are mostly related to the reliability and accuracy of the flow rate measurement of the permeate stream especially in the case of low permeate flowrates.

- Most of the flow measurement equipment causes pressure drop that changes the transmembrane pressure. It is recommended to install a pressure sensor on the permeate side.
- Generally, the flow measurement equipment are calibrated for one compound and conversion factors are applied for other gaseous compounds.
- Avoiding contamination of the permeate gas stream during flow measurement prior to analysis.
- Using gas independent pressure sensors with high accuracy and narrower possible range.
- Apply appropriate heating/temperature control on the feed side.

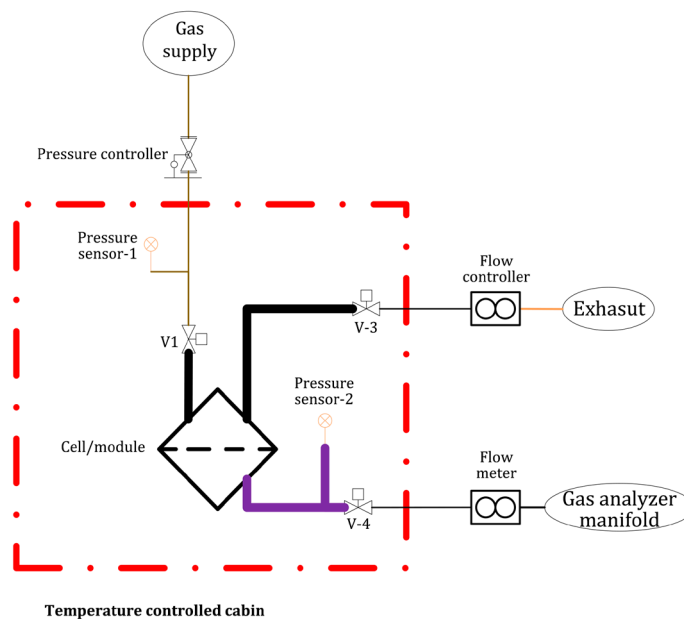


Figure 2 — General design of a variable flowrate, fixed pressure apparatus

The permance is determined according to:

$$L = \frac{\dot{n}_p}{A \cdot (f_R - f_p)}$$

where

L is the permance

- A is the active membrane area
- \dot{n}_p is the molar permeate flowrate
- f_R is the fugacity on the feed/retentate side
- f_p is the fugacity on the permeate side

The latter two variables can be replaced by the pressure in case the validity of the ideal gas law can be assumed. The molar flowrate can be calculated from the measurement value supplied by the flowmeter. This typically either is the volumetric or the mass flowrate. The former again involving the use of an appropriate equation of state, the latter is determined by dividing the measured value by the molecular weight.

8 Mixed gas permeation

8.1 General

The mixed gas permeation performance described in this clause relates to the entire membrane. In case of asymmetric membranes as described in subclause 6.2 this means the measured values entail not only the performance of the actual separation layer but also those of possible non-woven supports, porous support layers as well as gutter and protection layers.

8.2 List of gas mixtures

Relevant gas mixtures represented by binary approximations for the assessment of membrane performance for gas mixtures are:

- Air separation: Oxygen/Nitrogen ($y_{O_2} = 21 \text{ mol-}\%$)
- Biogas and natural gas treatment: Carbon dioxide/Methane ($y_{CO_2} = 40 - 50 \text{ mol-}\%$)
- Flue gas treatment: Carbon dioxide/Nitrogen ($y_{CO_2} = 15 - 30 \text{ mol-}\%$)
- Ammonia production: Hydrogen/Nitrogen
- Refinery gas treatment: Hydrogen/Methane
- Synthesis gas: Hydrogen/Carbon monoxide
- Synthesis gas: Hydrogen/ Carbon dioxide
- Natural gas treatment: n-Butane/Methane ($y_{n-C_4H_{10}} = 5 \text{ mol-}\%$)
- Gas drying: Water vapour/Nitrogen
- Helium recovery from natural gas: Helium/Methane
- Olefins/paraffins: Ethylene/Ethane and Propylene/Propane

This list is not exhaustive. It is meant to provide to give an indication of typical separation tasks solved using gas permeation processes.

8.3 Constant volume-variable pressure method (CVVPM)

The procedure is in general as described in Clause 7. In case of mix gas permeation measurements, the collected permeate sample is needed to be analysed. The most common sampling procedure is: expanding the sample to a gas chromatograph (GC) sampling loop that is kept under vacuum prior to the sampling. The permeate could also be pressurized with the carrier gas of the GC and expand to GC loop without vacuum applied on the loop. In case of mix gas permeation measurements with highly selective membrane samples are tested, be aware that small errors in gas analysis may cause large errors in the results. It is recommended to validate the gas analysis equipment and procedure and perform single gas measurements besides the mix gas ones. Additional points compared to single gas permeation experiments are:

- the composition of the permeate gas should also reach to a steady state besides the slope value,
- using a cell/module design that prevents concentration polarization on the feed side due to stagnant spots within the upstream side of the cell/module.

8.4 Variable flow, fixed pressure method

8.4.1 General

The measurement is conducted as described in subclause 7.4. The permeate stream or part of it is directed to a gas analyzer in this case. Exact determinations of feed and retentate compositions are generally also required. The following, additional points should be considered:

- Flow measurement using devices calibrated for a certain single gas creates a lot of complexity. Apply appropriate methods as typically given by the manufacturers of the flow measurement devices.
- The feed flowrates are generally higher for these measurements in case of mix gas permeation measurements, hence appropriate heating/temperature control on the feed side should be applied.
- A possible influence of concentration polarization on the experimental results should be avoided. This can be ensured by increasing the feed flowrate at otherwise constant operating conditions and monitoring the permeate flowrate. In case the deviation of successive values does not exceed the accuracy range of the employed flow measurement devices, it can be assumed that the impact of concentration polarisation on the measured flowrate value is negligible.
- The flowrate on the feed side should be much greater than that of the permeate. Typically, two orders of magnitude should be applied. There are two main reasons for this. A high enough flowrate will give rise to a high flow velocity and hence allow for minimization of any concentration gradients between the bulk of the feed side flow and the membrane surface. I.e., the influence of concentration polarization on apparent, measured permeances can be considered negligible. Furthermore, a high enough flowrate will minimize composition differences between feed and retentate. Hence, the composition can be considered uniform on the feed/retentate side of the test cell or module. Alternatively, mean values (arithmetic or logarithmic) or a mathematical model accounting for the change in composition along the membrane surface have to be applied.

The permeances of the individual component i can be calculated according to:

$$L_i = \frac{\dot{n}_{P,i}}{A \cdot (f_{FR,i} - f_{P,i})}$$

where

L_i is the permeance

- A is the active membrane area
- $\dot{n}_{p,i}$ is the molar permeate flowrate
- $f_{FR,i}$ is the fugacity on the feed/retentate side
- $f_{p,i}$ is the fugacity on the permeate side

The latter two variables can be replaced by the partial pressure in case the validity of the ideal gas law can be assumed. $\dot{n}_{p,i}$ can be calculated by multiplying permeate flowrate by the permeate mole fraction of the considered component. The molar flowrate can be calculated from the measurement value supplied by the flowmeter. This typically is either the volumetric or the mass flowrate. The former again involving the use of an appropriate equation of state, the latter is determined by dividing the measured value by the molecular weight. In case feed and retentate fugacity show a deviation of larger than 5 % (related to the feed value) mean values or a model should be employed. The arithmetic mean value is:

$$f_{FR,i} = 0,5 \cdot (f_{F,i} + f_{R,i})$$

The logarithmic mean value is:

$$f_{FR,i} = \frac{f_{M,i} - f_{R,i}}{\ln \frac{f_{F,i}}{f_{R,i}}}$$

The description of a mathematical model is beyond the scope of this document.

8.4.2 Controlled evaporation

There are several possibilities to prepare gaseous feed mixtures that contain components which would be in their liquid state at the selected temperature and pressure. The foremost example is water vapour, but also hydrocarbon and solvent vapours are often considered. One option to prepare such a mixture is to feed liquid phase and gaseous feed components at ambient temperature but operating pressure into an evaporation system where the required heat of evaporation is fed into the two phase feed stream, thereby evaporating the liquid content and supplying a mixed gas feed. The resulting feed composition should always be controlled using an appropriate means of composition analysis as e.g. gas chromatography.

8.4.3 Saturation methods

Saturation methods allow for the gas phase supplied to the measurement system to enter a liquid phase reservoir. The gas phase exiting the reservoir will contain vapour of the liquid it just passed through. The maximum being determined by thermodynamic equilibrium between the gas and liquid phases at the given temperature and pressure. The resulting feed composition should always be controlled using an appropriate means of composition analysis as e.g. gas chromatography.

8.5 Guidelines to ensure measurements of intrinsic membrane properties

8.5.1 Membrane pretreatment to remove any remainders of membrane preparation history

It should be ensured that membranes to be tested do not contain contaminants that will affect the measured values. Typical such contaminants could be solvents. These contaminants can be removed from symmetric membranes by placing them into a fume cupboard for a long enough period of time. Increasing the temperature might also be of help. Integrally skinned, asymmetric membranes can be subjected to heat treatment as part of the production process as can thin film composite membranes. Asymmetric membranes exhibiting a permeance high enough to be measured by flowmeters for specific gases should be investigated according to subclause 7.4 at ambient temperature and permeate pressure in regular intervals as e.g. once per day. In case the deviation of successive values does not exceed the accuracy range of the employed flow measurement devices, the membrane can be assumed to be free of

contamination. The described procedure also serves to ensure that the measured results are not affected by aging.

8.5.2 Testing repetition under the same conditions with either the same membrane sample or different membrane samples obtained in the same membrane preparation conditions

Ideally, more than one membrane sample of a membrane production batch should be investigated. Furthermore, the experiments should be repeated two times in order to be sufficiently accurate.

8.5.3 Testing of membrane stability and potential aging

The membrane should be re-investigated at the conditions imposed for the first experiment. This will elucidate, whether the membrane was stable under the experimental conditions it was exposed to and whether it was still subject to aging.

8.6 Guidelines for composition analysis

Typically, the testing of the separation of a given mixture requires the use of a gas chromatograph (GC, or analogous system) to determine the concentrations (upon previous calibration of the GC) of the species at both permeate and retentate sides to determine driving forces for every gas component. These concentrations and driving forces, together with the knowledge of the feed, retentate and permeate flows and the membrane area, will be used to calculate component permeabilities or permeances, depending on the membrane structure. The presented permeabilities and permeances should be supported by suitable statistical treatment derived from the repetition of the measurements with different membrane samples prepared in the same conditions or obtained from the same batch.

9 Reporting and models

9.1 Reporting

For reporting, the following data should be supplied format:

1. Type of membrane
 - a. Material (section 4)
 - b. Geometry (section 5)
 - c. Morphology (section 6)
 - d. Membrane area
2. Method applied to assess permeation performance (sections 7 and 8)
 - a. Single gas or mixture
 - b. Which single gases / mixtures were employed in what order
 - c. Temperature, pressure and, if applicable, composition ranges
 - d. Types and accuracy of equipment employed for temperature, pressure and composition measurement
3. Quality parameters
 - a. Number of repetition of experiments

- b. Number of samples of production batch
- c. Tested for aging
- d. Tested for contaminants remaining after production
- e. Tested for influence of concentration polarisation if mixed gas measurement
- f. Feed flowrate two orders of magnitude larger than permeate flowrate (variable flow, fixed pressure method) in order to prevent composition profile developing between feed and retentate

A way of reporting measured data is a csv format file [13]. For single gas data (Clause 7), it would contain at least four columns: temperature in K, feed pressure in Pa, permeate pressure in Pa and permeance $\text{mol/m}^2/\text{Pa}/\text{s}$. In case of mixed gas measurements, additionally the compositions of feed, retentate (see point 3 f) above) and permeate for each experiment need to be provided.

9.2 Recommended models

The data reported in this way is sufficient to estimate parameters of models commonly employed to describe the permeation of gases and vapours through membranes. Examples are the solution-diffusion model, Arrhenius type models, the Free-Volume model and Sievert's law.

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