

## 5 Mixtures of Pure Gases

In this chapter we will deal with the production of gas mixtures in gas cylinders. Here the components should be in the gas phase and the associated pressure can be up to 300 bars. The production of cylinders with virtually no pressure for analytical calibration is briefly touched upon in point 7.1. Likewise, the methods for production for the user of mixtures with virtually no pressure are given in point 8.3.

The physics of gas mixtures was introduced in paragraph 2.3 in the main features. The production of gas mixtures occurred after the Second World War mainly based on the measurement of pressure with exact volumes. Nevertheless, it was necessary to include the real behaviour of the gases in the calculation. Since the availability of precise scales, direct relation became possible to the mass and therefore the SI basis. Because a component in a gas mixture is measured by mass regardless of pressure and temperature, no correlations are necessary by means of the real gas factor. The calculation of the ideal volume for a gas G is carried out based on the Molecular weight  $M_{G,Mol}$  and the ideal volume  $V_{STP}$  as is. The certification of the composition of the gas mixture is carried out on this basis. Nevertheless, the actual pressure should be controlled due to industrial safety. For the calculation based on the real gas factor, see example E2.3-1.

The following information is necessary for the characterization of a gas mixture:

- Composition in material amounts, volume fraction, or mass fraction. The composition is mostly certified based on measurement of a physico-chemical value.
- The error in %-rel. from the analytical value, see para. 7.2.
- Purity of the source components, if necessary guaranteed through the measurement of the concentration in the final components. The limitation of moisture content is frequent.
- The stability statement as the minimum time from the production date of the test gas that the measured value can be used see para. 7.2.

The user gives a target specification for the gas mixture with his order; the producer guarantees the adherence to the blending tolerance.

*Example E5-1: Gas mixture Helium with 4 % O<sub>2</sub> and 150 ppm CH<sub>4</sub>, specified as Mol/Mol. The producer guarantees for 4 % O<sub>2</sub> a blending tolerance of 5 %-rel. as well as an analytical certainty of 1 %-rel., accordingly for the 150 ppm CH<sub>4</sub> 10 %-rel. and 3 %-rel.*

*The analyzed mixture is delivered with the following composition: 4.15 % O<sub>2</sub>, 138 ppm CH<sub>4</sub>. The evaluation must result from the correlation between the blending tolerance and analytical accuracy.*

*In the case of the O<sub>2</sub> – content, 4.15 % ± 1 %-rel. signifies: the actual concentration value lies between 4.11 and 4.19 % O<sub>2</sub> (values rounded). The measured value and the true value lie within the guaranteed blending tolerance from 3.8 to 4.2 % O<sub>2</sub>.*

*With methane, the following situation arises: 138 ppm ± 3 %-rel. for the analytical value, this corresponds to a rounded concentration range from 134 to 142 ppm. The lower value does not lie within the blending tolerance range from 135 to 165 ppm. On the other hand, the measured value is sufficiently placed. For many applications, this difference is marginal; with high demands for quality e.g. the testing of exhaust gas from automobile industry it should not be neglected.*

Gas mixtures are required not only for the calibration of analytical instruments, but also for material applications. For both types, the precision required has risen steadily over the recent years. Because normally the homogenised gas mixture fabricated in a suitable procedure must be tested by means of a physical or chemical method. The target-performance comparison must also be considered. This is included in the area of the metrological (instrumentation) certainty which is taken up in para. 7.1. Gas mixtures which serve as standard are often called calibration gas mixtures. Their certification is reserved to national or nationally accredited facilities. The gas mixtures used thereby are called test or calibration gases.

In the USA the National Institute of Standards and Technology (NIST) establish certification. Standard gases sold by NIST are called Standard Reference Materials (SRM). Gas manufacturers may produce NIST Traceable Reference Materials (NRTM). Other standards may be purchased from other national agencies such as the Netherlands NMI.

## **5.1 Static Procedures**

With the static procedures the gases are inserted successively into the cylinder or the volumes that were filled individually are combined. An additional mixing, often called homogenization, or the so-called rolling, is a necessary rule.

On the other hand with the dynamic procedures two or more gases are mixed at the correct concentrations while flowing and are immediately filled into the gas cylinder, most often by means of a compressor.

### **5.1.1 Gravimetric Procedure**

The first pictures, which showed compressed gas cylinders on beam scales, were to be seen in the late 70's. Nevertheless, this was no gravimetric procedure but rather a gravimetric confirmation of the composition because the mixtures were

produced mostly manometrically (by pressure). Before the first and after every following addition of a gas, the cylinder would be disconnected from the filling manifold and weighed. The data obtained through large balance accuracy were clearly better than the results achieved by analysis through a comparative process, e.g. dilution by means of gas blenders.

*Example E5.1.1-1: Balance mechanism in 1978 in the Specialty Gas Plant of the company Messer Griesheim GmbH/Germany, (Grefer et al 1978).*



**Illustration P5.1.1-1:** Beam balance, taken from (Grefer et al. 1978).

Data of the scales: Loading capacity 100 kg, precision  $\pm 20$  mg. The weights were put on by hand. A mix of 2%  $\text{CO}_2$  in CO could be certified with a relative error of  $\pm 0.2\%$ -rel.

*The weighing on beam balances always takes place against a compressed gas cylinder of the same design. Thus errors caused by the buoyancy in atmospheric air are usually avoided. The scales should be in a dust-free and air conditioned room. The compressed gas cylinders used must exhibit a flawless internal and external condition; loose paint residue can rapidly lead to additional errors.*

The principles of this kind of the mass determination have remained unmodified up to now, the accuracy has further increased; see among other things (Wilde 1988). Newer data about the methodology and the analysis of errors as well as examples can be found in (ISO 6142 2001). The three most important errors are:

- The error of the weighings, which is caused primarily by the inaccuracies of the balance. It can be reduced by repeated weighings.
- The uncertainty in the purity. As already discussed in the introduction, this is usually only represented in the type “greater than 5.0”. Then it is to be set for the contents

$$G_R \pm \Delta G_R = 99.999 \% \pm 0.0005\%$$

Here the error is half the difference from the content to 100%.

- The uncertainty of the molecular weight. Given in the data sheets for arsine  $M_{\text{Mol}} = 77.95 \text{ g} \cdot \text{mol}^{-1}$ . Provided that no more precise information about the value is given, one uses the error  $\pm 1$  in this digit place.

$$M_{\text{Mol,AsH}_3} \pm \Delta M_{\text{Mol,AsH}_3} = 77.95 \pm 0.01 \left[ \text{g} \cdot \text{mol}^{-1} \right]$$

Experiences and possible errors related to the production of precision gas mixtures using highly accurate beam scales were reported by (Heller 1992) and (Gaier u. Heller 1998).

If one proceeds with a light steel cylinder with a volume of 50 l and a working pressure of 200 bar, one must connect an empty cylinder weighing 65 kg. This demonstrates one of the negative sides of the trade of compressed gas cylinders: the unfavourable relation of product mass to the total mass. In our case, the relation is  $11.7 : 76.7 \cong 1 : 6.6$ .

*Example E5.1.1-2: The correlation between an initially weighed-in quantity to the resolution of the scale.*

*If a mixture of 1 %  $O_2$  ( $\varphi = 1.34 \text{ kg} \cdot \text{m}^{-3}$ ) in a 50l-cylinder with 200 bar working pressure is desired  $0.1 \text{ m}^3 = 0.134 \text{ kg}$  is to be weighed-in. Because a production tolerance of 5 % (= 0.0067 kg) has to be met, the resolution of the scale should be better than 6.7 g. Thus the real gravimetric production began only with the availability of single-pan balances of sufficient resolution in the load range of 100 kg.*

*In comparison to this, if a mixture of 0.01% = 100 ppm is required, then the initially weighed-in quantity is only  $0.00134 \text{ kg} = 1.34 \text{ g}$  and the resolution should be better than 0.067 g = 67 mg. If this is not to be achieved with available scales, a premixture (also called intermediate mixture) with the same gas type can be manufactured with the same components as the target mixture, whose concentration exhibits a favourable intermediate value. In our case a 1% premixture would be very suitable.*

*Example E5.1.1-3: Data from modern, single-pan electronic balances. The information in the following table was put together by Mettler-Toledo GmbH, Greifensee/Switzerland*

**Table 5.1.1-1:** Scales for the gravimetric production.

Suitable for the cylinder size [l]	Maximum load in [kg]	Readability (resolution) in [g]	Suitable for explosion protection
10	32	0.1	yes
50	150	1	yes
12x50 *	1500	20	yes

\*in the pallet: single cylinders, in bundles firmly secured.

Before the following details are to be applied to gas mixing stations and the principle of re-weighing, special attention needs to be paid to the liquid mixtures, see e.g. (Air Liquide 2005). These include mixtures at ambient temperature containing a combination of liquefied gases and liquids. The characteristics of these excluded mixtures which can be produced gravimetrically are:

- The composition of the liquid and gas phase is different and dependent on temperature.
- The composition changes with the withdrawal.
- A filling factor in kg/l of an authorized institute must be present for the liquid mixture concerned, e.g. in Germany through the Bundesanstalt für Materialprüfung (BAM).
- With the presence of a double-valve with tubing, the mixture can be withdrawn both gas-phase as well as liquid.

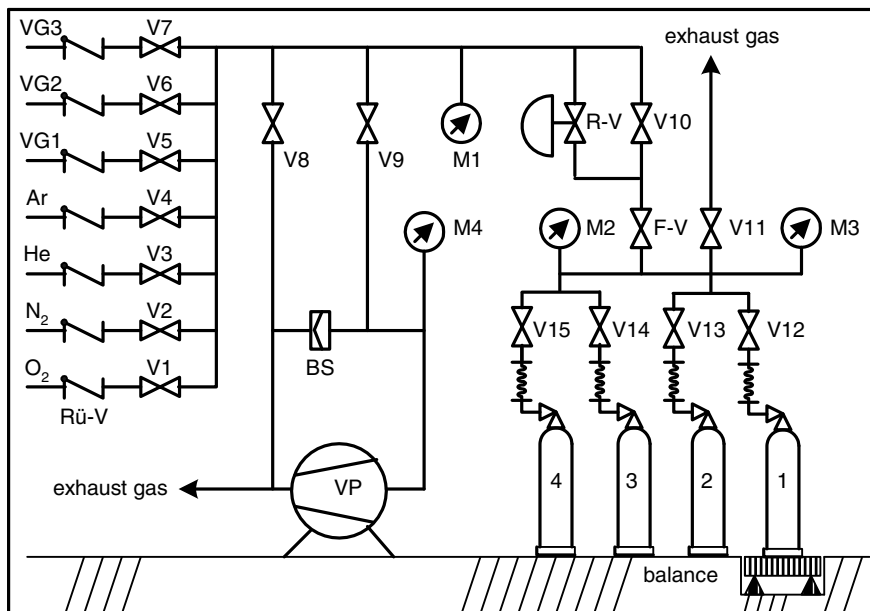
### 5.1.1.1 Principle of Gas Mixing Stations (Manifolds)

The principle of the gas mixing manifold can be seen in Illustration P5.1.1.1-1 on the next page.

For the supply, the three inert gases N<sub>2</sub>, He, and Ar as well as O<sub>2</sub> were selected. Furthermore, the possibility for up to three premixtures, PM1 to 3 exists. With these connections, another gas, e.g. Kr or N<sub>2</sub>O can be connected, of course. In the selected example, one should strictly exclude the use of a cylinder with flammable contents since O<sub>2</sub> is available at high pressure. This principle also applies vice versa to manifolds in which flammable gases are used. In these cases O<sub>2</sub> and other oxidising gases are to be excluded. The same principle applies similarly with acid and basic gases. For instance, HCl and NH<sub>3</sub> are to be avoided in a gas mixing manifold!

The available gases or premixes are supplied to the regulating valve R-V and the parallel valve V10. In the simplest case, the R-V is a needle valve. Since the purging process cannot take place sufficiently *via* the R-V, a parallel valve is recommended. On the way to the compressed gas containers 1 to 4, the fill valve F-V can be found. From here, the pipe lengths to the cylinders should be the same to prevent longer pressure settle-times after the addition of each component. Given the maximum allowable concentration deviation of 0.1%-rel. between the cylinders, pressure settle-times of 5 to 15 minutes are not unusual. They must be determined separately for each installation type. The parallel filling was planned for up to 4 cylinders, which can be isolated individually by valves V12 to V15.

The cylinders should be evacuated; because of time limitations the use of the vacuum pump VP at the manifold should be restricted to residual evacuation of the cylinders.



**Illustration P5.1.1.1-1:** Principle of a manually operated gas mixing manifold.

Cylinder 1 with isolation valve V12 is put on the scale embedded in the floor. The mass of the evacuated cylinder 1 is to be determined and creates the initial value for the following inputs according to the recipe. For the calculation of these, see the example E2.3-1.

Before changing each gas type, F-V must be closed. The pressure venting of the manifold between valves V1 to V9 and F-V is through V8. The evacuation occurs through V9. It is recommended that one conducts at least one purging with each new component followed by a pressure venting and evacuation.

The pressure gauges M1 and M2 are important to the filling process, which can only take place when M1 indicates a higher pressure than M2. Otherwise, an uncontrolled back-flow takes place most often causing the gas mixture to be rejected. M3 is intended as a positive pressure safety device. The manifold can be automated if control valves are used.

*Example E5.1.1.1-1: The filling cabinet of the Linde AG Speciality Gas Plant in Unterschleißheim. Photos Mettler-Toledo GmbH, published in the magazine (Mettler-Toledo 2001).*



**Illustration P5.1.1.1-2:** View in a filling cabinet.



**Abb. Illustration P5.1.1.1-3:** View of the operating side of the filling cabinet.

*Illustrations P5.1.1.1-2 and -3 show the filling manifold for the production of flammable mixtures which came into operation in the year 2000.*

*Two Metler-scales with 32 and 150 kg maximum capacity are installed in the ground, 11 cylinders of either 10 or 50 litres can be filled in parallel. In addition, a vacuum pump on the rear wall and a metering device (Example E5.1.2-1) for liquid injections can be detected on the right hand side. The cabinet has a roll-up door that is locked when  $p > 10$  bar and has its own air inlet and exhaust. On the operations side: In the upper box are the valve controllers. With the control unit ID7 from Mettler-Toledo beneath.*

### 5.1.1.2 Re-Weighing (Also Referred to as Back-Weighing)

When looking at filling and analytical control from a distance, an anachronism becomes apparent: The measured value determination is based on mixtures whose mass was determined very precisely by means of re-weighing. The calibration gases are produced gravimetrically, the initially weighed-in quantities adhere to the blending tolerance. A manually complex re-weighing is only accomplished if the customer or additional interests require these data. However, the resolution of modern scales would be sufficient with re-weighing for a certification based on the mass determination for many calibration gases and thus the need for physico-chemical measurements would be reduced significantly.

An easily automated, patented solution has been indicated (Schön 1996)<sup>1</sup>. This consists of:

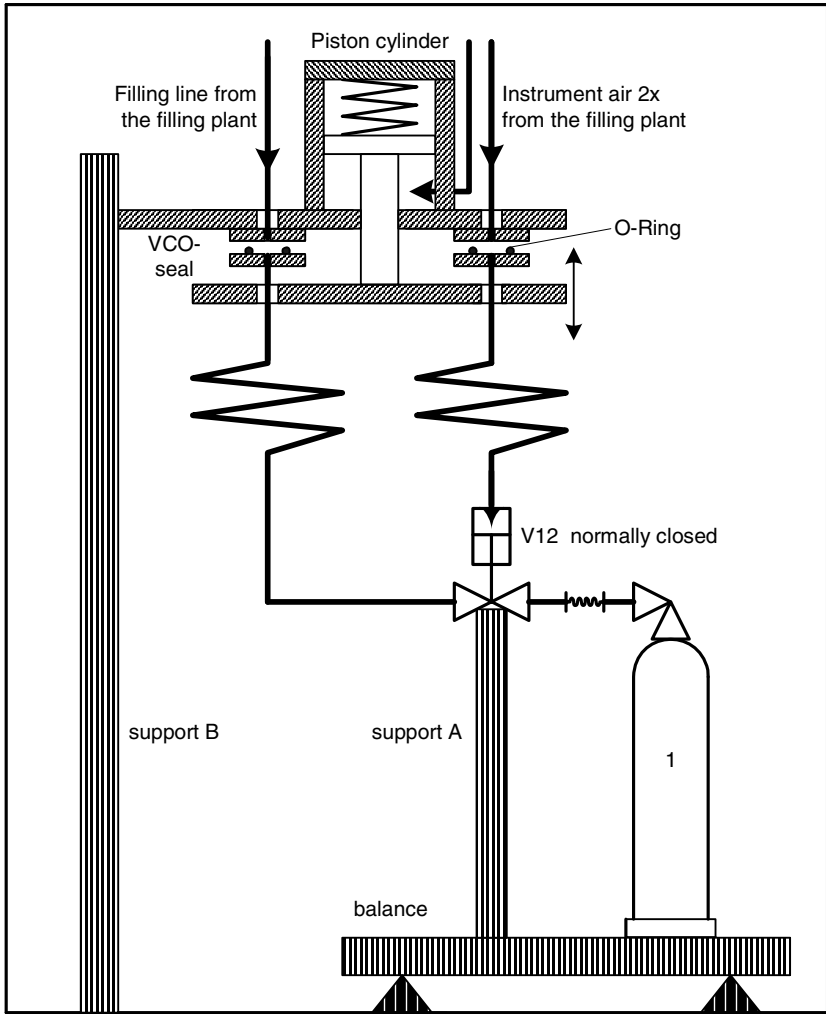
- A control valve which is firmly connected to the scale and is attached to the compressed gas cylinder to be filled.
- An adjustment element which can be detached and closed. In the open position, a portion remains on the scale while the other portion belongs to the fill plant. Thus, the desired isolation of the filling line is achieved.

Fig. P5.1.1.2-1 shows a simple solution in this sense. A gas cylinder 1 is connected to valve V12 which is closely connected by support A over the scale. The name V12 was chosen because this system fits directly into the gas mixing schematic in Fig. P5.1.1.1-1. V12 is a pneumatically controlled valve with a normally state closed. Now two more lines are necessary for the remaining gas mixing arrangement: the filling line and the instrument air (working air). The heart of the manifold is two detachable connections for which the VCO seals with O-Rings from the product range of the Swagelok Company are suitable. A pneumatic piston cylinder is firmly connected by support B to the floor. The upper portion of the VCO seals is firmly attached to this as well. The lower portions are kept flexible by the filling and air line, which is indicated by coils in the drawing. The piston cylinder can only close or open both VCO seals together. Instead of a piston cylinder, one can also use double-acting pneumatic or electrically operated cylinders. The operations are:

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<sup>1</sup> The European Patent is in the possession of Linde AG





**Illustration P5.1.1.2-1:** Schematic representation of the re-weighing.

- A: The seals are closed, V12 is open like the cylinder valve, which is evacuated. Then V12 is closed, the filling line and the working air line are brought to atmospheric pressure. The disconnection and weighing of the cylinder follow.
- B: The VCO-seals are closed; the filling line up to V12 is evacuated. After opening V12, the first (smallest) component is introduced.
- C: V12 is closed; the filling and working air lines are relieved. The VCO-seals are opened. The weighing of the first component then takes place.
- D: The introduction of the next components and the mass measurements take place as in Step C.

- E: After the filling of the last component, the gas cylinder valve is closed and after venting the filling line from V12, the cylinder is removed from the scale.

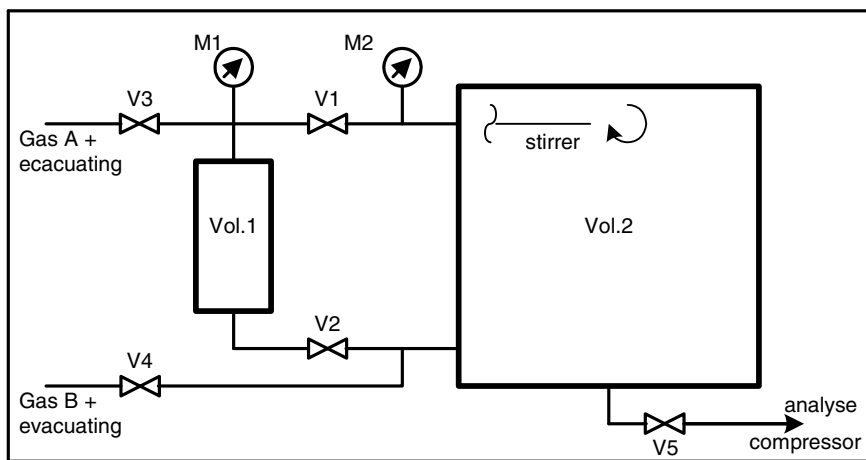
### 5.1.2 Manometric and Volumetric Procedures

A significant number of manometric (by pressure) and volumetric procedures as well as combinations of both have been developed. Descriptions can be taken from the article of (Hamann et Riedel 1980) as well as the standards (ISO 6146 1979, withdrawn) and (ISO 6144 2003). As already described, their meaning has rapidly diminished.

The traditional manometric procedure can be described on the basis of Fig. P5.1.1.1-1. In the sequence of events, one imagines the scale shut-down and the Pressure Gauge M2 replaced by several very precise pressure transducers for different pressure ranges. The addition of components takes place as described up to the pre-calculated pressures. A significant warming of the gas cylinder normally only occurs with higher pressures. This often assessable temperature rise must be considered with the default pressure. Another method consists of filling the main component up to an intermediate pressure close to the expected pressure. A temperature sensor on the cylinder gives the data for recalculation and, on this basis is further filled to the final pressure.

A purely volumetric procedure occurs when two or more very precisely known volumes of different gases but at the same pressure are subsequently combined. This procedure is important for the analytical calibration.

One can obtain mixtures in the ppm-range by using volumes of different pressures. The principle is shown in the following fig.



**Illustration P5.1.2-1:** Principle of the volumetric-manometric procedure at low pressure.

Explanation: Both volumes, Vol. 1 and 2, must be determined very precisely including the tubing and fittings. It is favourable that the structural design occurs in such a way as to permit complete filling with water. Vol. 1 and 2 are evacuated individually through valves V3 and V4 and then filled with gases A and B up to the intended pressure. With work at low pressure and small masses of gas, a thermocouple is usually not necessary. The connection between the volumes is made through valves V1 and 2 as the pressures are equalized. An agitator is necessary for sufficient mixing. Now the mixture can be used through valve V5 either for analytical purposes or to be filled through a compressor into a compressed gas container.

As early as 1970, a mixture of 10 ppm could be produced using such an arrangement in a single step with an accuracy of better than 5 %-rel. if the following parameters were selected: Vol.1 = 1 l, Vol.2 = 1000 l, volumetric precision  $\pm 0.2$  %-rel., M1 and M2 mercury manometers with a reading precision of  $\pm 0.05$  mm Hg, measurement range from 15 to 1500 mm Hg abs. Such an installation and its operation require a great deal of effort for little productivity.

For the combination of the volumetric-manometric with the gravimetric, the following examples were selected.

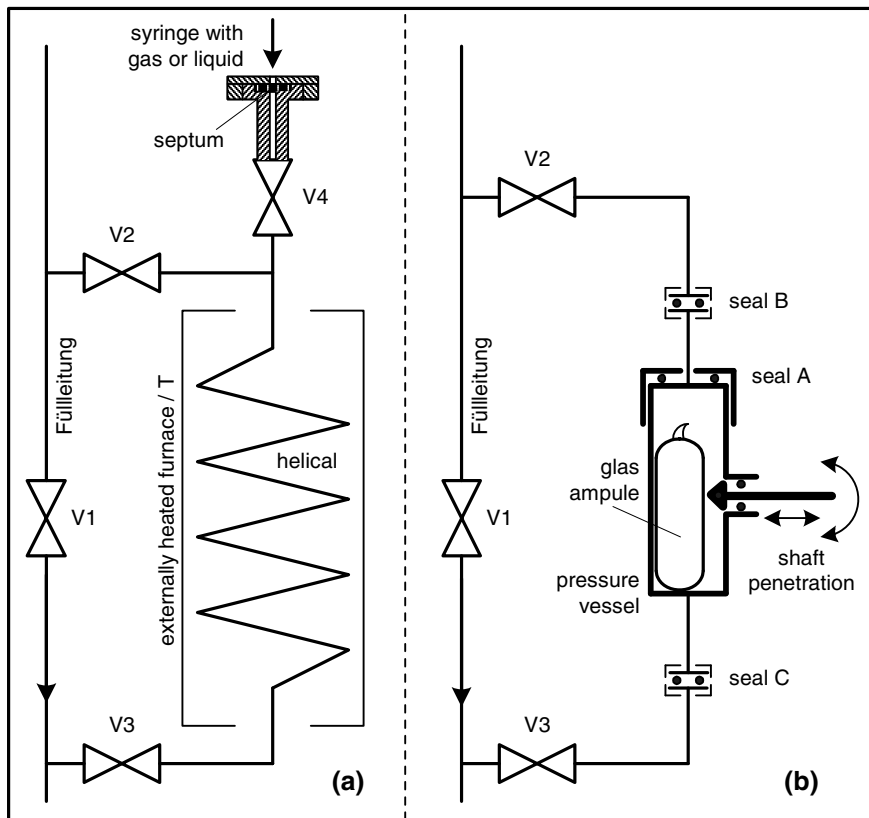
*Example E5.1.2-1: Possible retrofit installations for a gravimetric mixing manifold, as illustrated in Fig. P5.1.2-2.*

*Explanation (a): The use of gas-tight syringes is well-known from gas and liquid chromatography. With valve V4 open and V1 and V2 closed, the manifold including the product cylinder to be filled is under vacuum. With the syringe, the septum of soft plastic is punctured, through which gas or evaporating liquid reaches the manifold. V4 is then closed and the next component is introduced through the path V2 – coil – V3. Thus remnants of the injected substance are rinsed into the target cylinder. The coil is externally heated ( $T = 50$  to  $150^\circ\text{C}$ ) if hard-to-evaporate liquids are introduced. This also includes water.*

*The procedure becomes entirely gravimetric if in the case of liquids the syringe is weighed before and after the input. With gases, this procedure is usually excluded due to the small mass in the syringe.*

*Explanation (b): Principal item is a small receiver that can hold a glass ampoule. This is filled with a gas or liquid on a separate manifold under very special conditions. Examples are radioactive isotopes Kr-85 and H-3. The small receiver can be removed from the manifold with the detachable seals B and C shown with O-Ring seals. The container also has an additional seal A through which the ampoule can be inserted. The recommended seals are VCR, thus no realignment of the lines needs be accomplished and one achieves a low leak rate. The approach is analogous to example (a). The ampoule is destroyed by means of a rotating shaft through a sealed port while the manifold is under vacuum. This can be easily constructed by the upper portion of a needle valve. With gases, it is necessary to know the volume and pressure of the ampoule or another parameter, e.g. for Kr-85 the activity is Becquerel (Bq). With liquids, there is the possibility to use pre-weighed quantities if the mass of the ampoule is known.*

A related method is the use of a smaller receiver without seals C, but, with additional valves in the lines to seals B and C. Here, likewise, filling is possible on a separate manifold.



**Illustration P5.1.2-2:** The volumetric blending of defined masses of gas into a filling manifold for mixing.

### 5.1.3 Homogenization and Separation

If two or more gases are added successively into a gas pressure container, a homogenization (mixing) occurs. This is due to diffusion which has been discussed in para. 2.2.3. This homogenization can be completed in as short a time as a few minutes or taking several years. Examples of quick mixing are:

- Two or more light gases such as He and H<sub>2</sub> mix at 200 bar after approx. 30 minutes.
- If the lighter gas is introduced first, the heavier gas causes a rapid homogenization. It “falls” through the light and they swirl themselves together. Diffusion smoothes the local concentration gradients. A typical application: Synthetic air starting first with N<sub>2</sub> and then O<sub>2</sub>.

- The homogenisation takes place faster in shorter containers with larger diameters than in taller, narrow ones.
- Using a so-called mixing-tube. This is a dip-tube screwed-into the valve (similar to those used for the withdrawal of liquefied gases), but with a closed end and containing many small, laterally drilled-holes up to the end. During gas input, a steady distribution occurs along its axis. The disadvantage is the limited ability to evacuate the cylinder, so that this principle finds little use.

If one cannot determine a specific mixture by obligatory homogenization two methods present themselves:

- By rolling the cylinder around its axis, mechanical impulses are transferred to the particles which lead to turbulence due to inertia when stopping and reversing direction, thus promoting diffusion. One to one and a half minute in one direction is an appropriate turning time. The use of the so-called “mixing strips,” metal or plastic strips that lie loosely in the cylinder, are not recommended. Because they cause abrasion on the walls, the gas cylinder “mutates” and becomes a particle generator.
- The diffusion increases with warming of the cylinder. According to Equ. (2.2.3-8) it increases with  $T^{3/2}$ . A water bath up to a quarter of the cylinder (“foot bath”) is very effective because of convection forming in the cylinder.

With diffusion, the Entropy of the system increases. This arises from fundamental physical laws: In the absence of external physical forces, no separation occurs!

We have however, a terrestrial force to which every process is subject: the force resulting from the acceleration of gravity with  $g_{\text{Earth}} = 9.81 \text{ m} \cdot \text{s}^{-2}$ . In evaluating the influence, with a first look is taken at the average (kinetic) energy of a particle according to Eq. (3.4-1).

$$E_m = \frac{M_{\text{particle}}}{2} v_m^2 = \frac{3 \cdot R_{\text{Mol}} \cdot T}{2 \cdot k_{\text{Avogadro}}} = \frac{3 \cdot 8.31441}{2 \cdot 6.022 \cdot 10^{23}} T = 2.07 \cdot 10^{-23} \cdot T \quad [\text{J}]$$

The  $E_m$  depends only on temperature, but not upon the mass of the particle. Because of  $E_m$ , the particle moves in every direction.

The force  $F$  that acts upon the particle through the acceleration of gravity is calculated by the well-known formula “mass times acceleration.”

$$\begin{aligned} F &= M_{\text{particle}} \cdot g_{\text{earth}} = \frac{M_{\text{Mol}} \cdot g_{\text{earth}}}{k_{\text{Avogadro}}} \\ &= \frac{9.81}{6.022 \cdot 10^{23}} M_{\text{Mol}} = 1.63 \cdot 10^{-23} \cdot M_{\text{Mol}} \quad [\text{N}] \end{aligned} \quad (5.1.3-1)$$

One obtains the potential energy  $E_{\text{pot}}$  by multiplying  $F$  with the height of the particle ( $s$  in  $m$ ).

$$E_{\text{pot}} = F \cdot s = M_{\text{particle}} \cdot g_{\text{earth}} \cdot s = 1.63 \cdot 10^{-23} \cdot s \cdot M_{\text{Mol}} \quad [\text{J}] \quad (5.1.3-2)$$

*Example E5.1.3-1: Computation of the average kinetic and potential energy of  $H_2$  and  $CO_2$  at  $-20$  and  $+20^\circ C$  and a height  $s$ , which approximate the conditions in a 10-liter cylinder.*

*The temperatures are  $T = 253.15$  and  $T = 293.15$  K,  $M_{Mol,H_2} = 2.016 \cdot 10^{-3}$  kg and  $M_{Mol,CO_2} = 44.01 \cdot 10^{-3}$  kg. By using these in the above shown Eqs. one obtains*

$$\begin{aligned} - \quad -20^\circ C: & \quad E_m = 5.24 \cdot 10^{-21} \text{ J}, \quad E_{pot,H_2} = 3.29 \cdot 10^{-26} \text{ J}, \quad E_{pot,CO_2} = 7.17 \cdot 10^{-25} \text{ J} \\ - \quad +20^\circ C: & \quad E_m = 6.07 \cdot 10^{-21} \text{ J}, \quad E_{pot} \text{ invariably} \end{aligned}$$

*The resulting values for  $CO_2$  indicate that the average kinetic energy at the ambient temperature dominates in contrast to the average potential energy in a proportion of over 100:1, however, a change in the mixing proportion between the upper and lower portion of the cylinder cannot be excluded in principle.*

A calculation of the concentration differences results from the use of the barometric height formula. (Jessel 2001) has shown that for the most unfavourable case regarding concentration of a 50/50 mixture of  $H_2/CO_2$ , at a height of 1 m and  $20^\circ C$  as well as atmospheric pressure, the following deviation results

$$\frac{\Delta C}{C} = 85 \cdot 10^{-6} = 0.0085 \% \text{ -rel.}$$

This leads to  $C_{H_2} = 50.00425$  % and at the upper end = 49.99575 % at the lower one. If one uses a pressure of approx. 80 bar abs. for the 50/50 mixture, a small correction would be necessary due to the real behaviour of  $CO_2$ , which is however insignificant for our purposes. These resulting values cannot be verified with our current measuring technology. From this one concludes: The force of gravity has a negligible influence.

Note: If one could measure so precisely, one would thoroughly roll a test gas cylinder before sampling the gas mixture and then measure again with the cylinder in the horizontal position.

A decrease in temperature may lead to a separation in components if condensable components are present.

*Example E5.1.3-2: The mixture looked-at above,  $H_2:CO_2 = 50:50$  at 80 bar abs., is placed outside overnight at a temperature of about  $-5^\circ C$ . What must be considered and done?*

*The mixture was calculated with the condition of certain use above  $+10^\circ C$ . With the contents of 900 l N, the partial pressure composition of the mixture amounts to approximately 40 bar abs.  $H_2$  and 40 bar abs.  $CO_2$ . From Table T10.4.8. one obtains the vapour pressure of  $CO_2$  at  $-5^\circ C$  to be approximately 30.3 bar abs. and at  $+10^\circ C$  approximately 45.1 bar abs. That means that the mixture has about a 10 bar safety margin above the vapour pressure at  $+10^\circ C$ . But at  $-5^\circ C$  a portion of the  $CO_2$  will condense and a higher  $H_2$  concentration will result.*

*The cylinder is once again homogenized after heating in a water bath at 40 to  $50^\circ C$  for 2 to 3 hours.*

Usually, the computation limit for condensation (“Dew-point limit”) is prescribed with +5°C. In the USA a limit of 0°C (+32°F) is often used. All components occurring in the mixture are to be considered at the same time. If there is the risk of the test gas cylinders exposed to much lower temperatures during transportation (winter!) compared to the ones in the lab, then the calculation limit must be decreased, e.g. to -10°C.

### 5.1.4 Mixtures of Flammable and Oxidizing Gases

If flammable as well as oxidizing components should both be contained in a gas mixture, then during production it has to be asked whether the explosive range is reached. The fact that the completed mixture does not lie in this range is understood. Whoever brings these mixtures into commerce, an evaluation should be carried-out by an authorized institution. In Germany this is the Federal Institute for Material Testing (Bundesanstalt für Materialprüfung – BAM), Abt II. Chemical Safety Engineering. This organization also supported the following discussions. We will look at the first three examples. The %-data are material concentration, the container is a 10 l – cylinder in each case.

*Example E5.1.4-1: Gravimetric production of a mixture at a half of the Lower Explosive Limit (LEL) of H<sub>2</sub> in air, which is 4 %, the Upper Explosive Limit (UEL) is 77.0 %. For this mixture, there is an approval by BAM for production up to pressures of 150 bar.*

*Because the Hydrogen concentration is small, we proceed from a premixture PM containing 49.9% H<sub>2</sub> in N<sub>2</sub>. The preweighed quantities M<sub>G</sub> were calculated as in example E2.3-1.*

**Table T5.1.4-1:** Prewighed quantities for the mixture 2% H<sub>2</sub> in air (N<sub>2</sub> : O<sub>2</sub> = 80 : 20).

Gas G	Concentration in [%]	Volume in [l]	M <sub>G</sub> in [g]
H <sub>2</sub> from PM	2.00	56.48	37.90
O <sub>2</sub>	19.60	276.18	394.29
N <sub>2</sub>	78.40	1076.43	1345.37

*Filling directly through the explosive range can be avoided with this mixture if one chooses the filling sequence H<sub>2</sub> + N<sub>2</sub> → homogenize → + O<sub>2</sub> → homogenize. The intermediate homogenization steps are absolutely necessary in order to prevent a location within the cylinder where an explosive mixture can develop. Note that O<sub>2</sub> is introduced at the end of the process at high pressure. Thus conditions are expected to be the same as if pure O<sub>2</sub> is handled. In particular, seals should be oxygen-compatible, also see further below.*

*Example E5.1.4-2: Gravimetric production of a mixture of 1 % O<sub>2</sub> in H<sub>2</sub>. LEL: 4.0 % H<sub>2</sub> in O<sub>2</sub>, UEL: 95.2 % (thus 4.8 % O<sub>2</sub> as LEL, related to the filling*

sequence  $O_2 \rightarrow H_2$ ). A BAM approval for this mixture allows production up to 100 bar.

**Table T5.1.4-2:** Prew weighed quantities for the mixture 1%  $O_2$  in  $H_2$ .

Gas G	Concentration in [%]	Volume in [l]	$M_G$ in [g]
$O_2$	1.00	8.89	12.70
$H_2$	99.00	880.49	79.20

With this mixture, one will choose the following sequence  $O_2 + H_2$  and will fill directly through the explosive range from LEL. It will exit this range if the “dilution” of the  $O_2$  with  $H_2$  reaches the value of 1:21, thus 22 bar abs. Homogenization is again necessary after completion of the filling.

*Example E5.1.4-3: Gravimetric filling of 60 %  $CH_4$  in air mixture. LEL: 4.4 %, UEL: 17.0 % . A BAM authorization is exists for this mixture at pressures up to be this 150 bar. Because the production has already led to problems, we will calculate it only for 30 bar.*

**Table T5.1.4-3:** Prew weighed quantities for the mixture 60%  $CH_4$  in air ( $N_2 : O_2 = 80 : 20$ ).

Gas G	Concentration in [%]	Volume in [l]	$M_G$ in [g]
$CH_4$	60.00	180.57	129.24
$O_2$	8.00	24.08	34.37
$N_2$	32.00*	96.30	120.36

If one chooses the filling sequence  $O_2 + N_2 \rightarrow$  Homogenize  $\rightarrow CH_4 \rightarrow$  Homogenize, then filling through the explosive range is inevitable. First 12 bar abs. is introduced, followed by the addition of the  $CH_4$ , an explosive mixture will result between 12.53 and 14.04 bar, assuming an ideal mixture. We have proceeded from filling pressure of 30 bar, to 150 bar, this sequence must be avoided because the explosive range will be traversed above 60 bar. And it generally applies: the higher the pressure of an explosive mixture, the greater the effect.

The following filling sequence is also conceivable:  $CH_4 +$  homogenized  $O_2/N_2$  - mixture. Locally combustible mixtures may develop; the filling of air however, is less dangerous than filling  $O_2$  as the last component under high pressure.

As seen, filling through the explosive range cannot always be excluded when producing mixtures with both flammable and oxidizing components. The following prioritization applies to generally prevent explosion and gas mixing:

- Primary explosion prevention: Avoid mixtures capable of explosion.
- Secondary explosion prevention: Avoid all forms of ignition sources.



- Constructive explosion prevention: Pressure resistant building method, protective chambers.

For the evaluation of explosivity of a mixture, the pressure and material dependencies of the explosive limits must be evaluated. In tables and safety data sheets, one usually only finds the values for atmospheric conditions with air as the oxidizing agent.

Now we turn to some concepts and models of explosion prevention. In addition, further details can be read in the monographs from (Bartknecht 1993) and (Steen 2000) safety-relevant numbers are from (Brandes u. Möller 2003) and (Molnár et al 2003). For the determination of explosive limits, see (EN 1839 2003).

The velocities at which the combustion processes spread in an explosive gas mixture lie between some  $\text{cm} \cdot \text{s}^{-1}$  and several  $\text{km} \cdot \text{s}^{-1}$ . Within the range of low velocities, for example with the Bunsen burner at  $40 \text{ cm} \cdot \text{s}^{-1}$  laminar flow occurs. This can also become turbulent with larger throughput. One calls both cases deflagration, or detonation, if it involves multiples of the speed of sound. As an example, for the  $\text{H}_2\text{-O}_2$ -detonating gas explosion, flame speeds of  $3 \text{ km} \cdot \text{s}^{-1}$  and temperatures over 3000 K can be measured. Explosion is the generic term for detonation and deflagration.

For a gas cylinder it is necessary to ask oneself what could be the ignition source for this closed system. There are two proven possibilities.

- a) Particles or also remnants of polymer seals or the like can be electrostatically charged in the cylinder by the gas flow during filling or also during withdrawal. If the cylinder is grounded, as is the case with the connection of a filling line, then sparking can result.
- b) If the oxygen concentration of a gas mixture is greater than 23 volume %, then many materials react differently than under atmospheric conditions, they burn more easily. Ignition can develop particularly with high pressures and pressure surges.

The author experienced two harmless cases of the formation of water from detonating gas during the production of calibration gas mixtures of the composition as in the example B5.1-4. In the first case the concentration of  $\text{O}_2$  could not be determined; an appropriate water vapour concentration in the cylinder could however. In the second case, a co-worker at the filling manifold noticed that the cylinder had already become very warm after only approx. 20 bar which occurs actually only after filling over 100 bar. The immediate investigation came to the same conclusion as in the first case. Here it had apparently concerned a virtually quiet deflagration, as the ignition source in both cases was only the electrostatic charging.

In two other cases the author has experienced detonations of light steel cylinders at distances of approx. 30 m, in which they were totally destroyed, fortunately but no personal injury occurred.

During the homogenization of an  $\text{Ar-O}_2\text{-H}_2$ -mix in a 10l-cylinder so-called plastic mixing-strips were used. The majority were twisted strips of  $200 \times 20 \times 2 \text{ mm}$ . Fortunately the roller was outside a filling building on a covered dock.

With the detonation about 600 cylinders were thrown from the dock, the roofing and roller were damaged, all windows facing the dock were shattered. Only individual pieces of the cylinder remained. The cause for the ignition was a reaction of  $O_2$  with the mixing strips, in addition these proved to be another flammable component in addition to the  $H_2$ .

During the gas input to a combustion manifold of a disposal system, an operational error resulted in the interconnection of cylinders which on the one hand contained large amounts of  $O_2$  and on the other  $H_2$ . It occurred during the introduction of high pressure. In the course of the detonation the building was severely damaged and burned. The author arrived within a few seconds after the explosion; it reminded him of an image he had experienced in 1943 after a bomb attack on the town centre of Munich. A part of a cylinder was found approx 50 m away in the roof of a delivery van. A likely ignition source was determined to be the effect of  $O_2$  on the seals in the cylinder with the  $H_2$ -component, which was not equipped with  $O_2$ -compatible materials.

It is asked about the energy, which is released during detonation in a gas cylinder, and the temperature rise and the increase of pressure. We use the calculation for ideal a gas as well as some highly simplified assumptions.

*Example E5.1.4-4: In a 10 l-cylinder at 15°C and 100 bar abs. is a  $H_2$ -Air-Mixture, whereby  $H_2$  and  $O_2$  are in the stoichiometric proportions. This represents the worst case. The cylinder has a working pressure of 200 bar. One would manufacture this mixture naturally only with a suicidal intention!*

*The relationship in air is for instance  $N_2$  (with 1% Ar, which is counted as  $N_2$ ):  $O_2 = 79:21$ . The stoichiometric relationship reads  $H_2 : O_2 = 2:1$ . From this  $H_2 : O_2 : N_2 = 42:21:79$  follows. From (D'Ans Lax 1983-98) one infers the value of  $242 \text{ kJ} \cdot \text{mol}^{-1}$  from  $\Delta H_{H_2O}$  for the water vapour as formation enthalpy at 20°C and 1013.25 mbar.*

*The data required for the further calculation in the cylinder have been arranged in the following table.*

**Table T5.1.4-4:** The  $H_2$ -Air-Mixture in the 10l-cylinder.  $v_G$  is the number of moles in a molar volume of 23.96 l at 15°C und 1 bar. The specific heat  $c_{v,G}$  at constant volume from the ideal kinetic gas theory. Real gases see a dependence  $c_{v,G}$  on temperature.

Gas G	$V_G$ in [m <sup>3</sup> ]	$v_G$ [number]	$c_{v,G}$ in [kJ · mol <sup>-1</sup> · K <sup>-1</sup> ]
H <sub>2</sub>	0.296	12.35	(3/2) R <sub>Mol</sub> = 0.0125
O <sub>2</sub>	0.148	6.18	0.0125
N <sub>2</sub>	0.556	23.21	0.0125
Sum	1.000	41.75	–
H <sub>2</sub> O	0.148	6.18	(6/2) R <sub>Mol</sub> = 0.0250

With the explosion 6.18 Mol of water vapour developed and an energy of

$$E = \Delta H_{\text{H}_2\text{O}} \cdot v_{\text{H}_2\text{O}} = 242 \cdot 6.18 = 1495.6 [\text{kJ}] = 0.415 [\text{kWh}] \quad (5.1.4-1)$$

has been released. This divides into radiation energy, which is transferred directly to the cylinder wall, and the amount of heat, which heats the gas in the cylinder and causes an increase in the pressure. There is no reliable data concerning the portions of both energy quantities.

If the detonation does not lead to a destruction of the cylinder, then all of the energy  $E$  must lead to a heating  $\Delta T_{\text{cylinder}}$  of the cylinder.

We take the heat capacity of iron  $c_{\text{Fe}} = 0.465 \text{ kJ} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}$  at  $25^\circ\text{C}$  from a table like (D'Ans Lax 1983-98). We will dispense with the small correction of the value from  $15^\circ\text{C}$ . The mass of the cylinder of 10 kg without a valve is taken from table T6.1.1. The cylinder valve is  $M_{\text{cylinder}} = 10.3 \text{ kg}$ .

$$\Delta T_{\text{cylinder}} = \frac{E}{M_{\text{cylinder}} \cdot c_{\text{Fe}}} = \frac{1495.6}{10.3 \cdot 0.465} = 312 [\text{K}] \quad (5.1.4-2)$$

This rise in temperature alone would not be sufficient in order to bring the cylinder from a pressure of 100 bar to bursting. However structural changes could occur in the steel or aluminium. If the portion of the radiation energy is only a few percent, then its contribution to the destruction of the cylinder is negligible.

We still have 29.39 Mol of gas in the cylinder from the evolution of water vapour and the remaining  $\text{N}_2$ . A  $c_{\text{V,mixture}}$  is calculated on the proportional distribution basis.

$$\begin{aligned} c_{\text{V,mixture}} &= \frac{v_{\text{H}_2\text{O}}}{v_{\text{H}_2\text{O}} + v_{\text{N}_2}} c_{\text{V,H}_2\text{O}} + \frac{v_{\text{N}_2}}{v_{\text{H}_2\text{O}} + v_{\text{N}_2}} c_{\text{V,N}_2} \\ &= \frac{6.18}{29.39} 0.0250 + \frac{23.21}{29.39} 0.0125 = 0.0151 [\text{kJ} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}] \end{aligned} \quad (5.1.4-3)$$

Analogously with Eq. (5.1.4-2)  $\Delta T_{\text{Gas}}$  can be calculated, whereby the  $E$  undivided is used.

$$\Delta T_{\text{Gas}} = \frac{E}{(v_{\text{H}_2\text{O}} + v_{\text{N}_2}) \cdot c_{\text{V,mixture}}} = \frac{1495.6}{29.39 \cdot 0.0151} = 3370 [\text{K}] \quad (5.1.4-4)$$

We proceed from  $T_1 = 288 \text{ K}$ , resulting in a  $T_2 = T_1 + \Delta T_{\text{Gas}} = 3658 \text{ K}$ . This value lies in the range of temperatures which have been measured in detonations. We calculate the pressure rise in the cylinder to  $p_2$  via Equ. (2.1-7) and  $V_1 = V_2 = V_{\text{geom}}$  as well as  $p_1 = 70.4 \text{ bar abs}$ .

$$p_2 = p_1 \frac{T_2}{T_1} = 70.4 \frac{3658}{288} = 894 [\text{bar}]$$

The calculated pressure lies within the range of the cylinder burst pressure given gas the test pressure of 300 bar. It should be considered that in the case of

*detonation, the pressure develops as a wave whose amplitude can be greater than the calculated one.*

If one carries-out this calculation with a starting pressure of 20 bar in Example E5.1.4-1, one calculates a  $p_2 = 179$  bar. A cylinder with a test pressure of 300 bar will withstand such a pressure shock. In this simple calculation it is neglected that at high temperature processes of dissociation (e.g.  $\text{H}_2\text{O} \rightarrow \text{H}^+ + \text{OH}^-$ ) take place, which consume energy and therefore decrease the temperature. On the other hand, the dissociation increases the number of moles and thus the pressure.

One can derive from this a rule of thumb can be derived: the explosion pressure in the cylinder may not exceed the test pressure.

In the deflagration, the maximum explosion pressure amounts to 8- to 10-fold the beginning pressure. Thus, during the filling process, the pressure passing through the explosion region should therefore not exceed 10% of the test pressure. As is known detonations cannot be counted on with higher inert gas concentrations. With no or only a slight inert gas concentration, the danger of detonation is clearly higher. Then the factor 10 is too low. This applies also to the following exceptions:

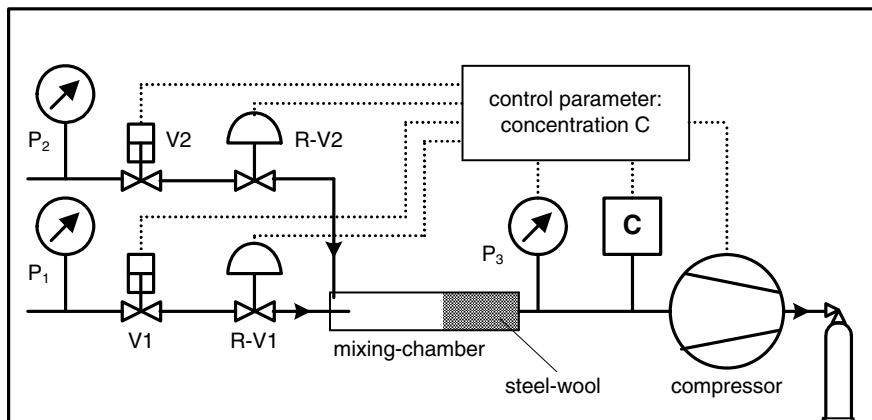
- Acetylene with its triple bond has a very large flammable region from 2.3 to 100 Vol-% in air, a low ignition temperature of 305 °C and may possibly dissociate explosively. This similarly applies to ethane, butadiene, and other chemically unstable gases.
- Laughing gas  $\text{N}_2\text{O}$  is oxidizing gas and supports combustion such as  $\text{O}_2$ , but when its bonds break, they release additional energy and through its decay, the number of moles increases resulting in a rise of pressure. The resulting explosion is more violent than with the oxidizers air or  $\text{O}_2$ .

Should it be discovered that a combustion process has taken place in a gas cylinder; a structural change in the cylinder material cannot be excluded. The result can be a tearing-open of the cylinder at a weak point after other pressure changes. Such a cylinder is to be removed from service and certainly scrapped.

Because the filling of reactive mixtures is very complex, when in doubt, consult a responsible institution, such as BAM in Germany.

## 5.2 Dynamic Process

These processes are used much less often in the production of gas mixtures in compressed gas cylinders than the static methods described above.



**Illustration P5.2-1:** Principle of a dynamic blending.

Explanation: Two gases 1 and 2 are supplied from lines under pressure  $p_1$  and  $p_2$ .

The purpose is to flow the desired relative volumetric flow rates of the two through suitable automatic controllers R-V1 and R-V2 which are supervised by means of the concentration measurement C. The volume flows must be mixed. A mixing chamber serves this purpose wherein one gas enters tangentially and one axially. In addition, in the outlet side of the chamber steel wool is advantageous for homogenization. There are also a significant number of good, patented mixing methods available. A compressor transports the mixture to the cylinder.

This procedure is only logical if there are a large number of cylinders to be filled because deviations from the desired value occur during the start-up process. The procedure has mostly been limited to simple mixtures with large blending tolerances e.g. nitrogen-hydrogen (forming gas) mixtures.

The Mass Flow Controller (MFC) will be discussed in para. 8.3. In recent years the range of application has expanded to both higher pressures up to 400 bar and mass flows to some  $100 \text{ m}^3 \cdot \text{h}^{-1}$ . Thus the MFC had also gained interest in industrial dynamic blending mixtures.

*Example E5.2-1: Dynamic Mixture with Linde in the USA. A tube trailer is to contain 22,000 ft<sup>3</sup> at STP (623 m<sup>3</sup>) of the food packaging mixture, 0.4% CO/35% CO<sub>2</sub>/N<sub>2</sub> at 950 psi (65.5 bar). The blending tolerance is 1% relative. Because the mixture has to be put into a tube-trailer where normal mixing techniques are not possible, this application is best suited to be blended dynamically.*

*As the installation of a dynamic blending system is complex and expensive, a system which can be flexible and utilised for a multitude of gases serves the best function. For this reason, the solution proposed uses components which can*

support other mixtures for cylinders or tube-trailers. The automatic controllers from P5.2.1 are Mass Flow Controllers. These are well suited for the application because they measure and control the flow of each gas component to a tight tolerance. The concentration differences warrant different sized MFC's to ensure adequate control.

Table T5.2 summarises the values for the controllers and flow rates. In this case are 0–10 l/min for CO, 0–500 l/min for CO<sub>2</sub> and 0–1000 l/min for N<sub>2</sub>. These are commercially available and can be purchased from one of a number of suppliers.

**Table 5.2-1:** Component specifications and flow rates for Example E5.2-1.

Gas G	Concentration C	Q <sub>v</sub> [l · min <sup>-1</sup> ]	Q <sub>v</sub> MFC [l · min <sup>-1</sup> ]
CO	0.004	5.7	0 – 10
CO <sub>2</sub>	0.350	496	0 – 500
N <sub>2</sub>	0.646	915	0 – 1000
Sum	1.000	1417	–

The concentration is measured through a micro-GC. This allows a rapid response to concentration changes.

A side note: Because this mixture contains CO and CO<sub>2</sub>, moisture must be kept at a minimum (< 0.5 ppm) to prevent the formation of iron pentacarbonyl. Additionally, the final pressure has specifically been reduced to lower the potential for the formation of this compound.