DEPARTMENT OF INORGANIC TECHNOLOGY

LABORATORY MANUAL

GAS SEPARATION USING HYBRID INORGANIC MEMBRANES

ICT Prague

Aim of the Study

The objective of this study is to examine the basic concepts of membrane gas separation and the effect of various process parameters on the overall membrane performance.

Introduction

In the last few decades membrane-based gas separation processes have gained extensive attention due to their numerous advantages in comparison with large-scale separation technologies (*i.e.* Pressure Swing Adsorption, Amine Absorption, Water Scrubbing, Cryogenic Distillation). Amongst a variety of available membranes, zeolitic materials gained specific attention due to their high open porous framework structures, large accessible pore volume and high CO_2 adsorption capacity. These features result in low footprint, low energy demand, low investment and operational cost, and consequently enable zeolitic materials to compete with currently available gas separation technologies.

In gas separation, a membrane is considered a semi-permeable barrier between two gas phases: a feed stream and a stripping medium (sweep gas or vacuum). The types of membranes employed for gas separation vary significantly (*e.g.*. dense, polymeric, hybrid etc) and thus determine the transport phenomena. For zeolitic materials (which are the case of this study), the mass transport is a combination of molecular sieving (size exclusion) and adsorption of compatible gas molecules in the membrane pores (surface diffusion). In addition, the governing of the mass transfer through these membranes also depends on the process operating parameters such as: (i) feed pressure, (ii) feed temperature, (iii) feed gas flow rate, and (iv) composition of the inlet gas.

The specific objective of this study is to determine the effect of various process conditions on the overall membrane performance in order to estimate the optimum operating regimes.

Theory

1. Transport Through Membranes

Knudsen diffusion

Knudsen diffusion takes place in the system where the pore diameter is comparable to the mean free path of the diffusing molecule, and thus the molecule-wall collisions dominate over molecule-molecule collisions.

Viscous flow

Viscous (Poiseuille) flow occurs when the mean free path of diffusing gas molecules is significantly smaller than the membrane. In this case molecule-molecule interactions govern the mass transport.

Slip flow

This type of the mass transport phenomena is a result of combined Knudsen and viscous flow that can be directly attributed to the non-uniformity of the membrane pores.

Surface diffusion

Surface diffusion occurs when the gas molecules are adsorbed on the pore walls of the membrane and migrate along the pore length. Surface diffusion increases the permeability of the preferably adsorbed species. As a result, the effective pore diameter is reduced restricting the passage of non-adsorbing molecules; this consequently increases the membrane selectivity.

2. Principle of Gas Chromatography

Gas chromatography (GC) is an analytical method that enables the identification and quantification of volatile compounds without their decomposition. In gas chromatography, the components of a sample are dissolved in a solvent and vaporised in order to separate the analytes by distributing the sample between two phases: a stationary phase and a mobile phase. The mobile phase is a chemically inert gas (*i.e.* helium, argon, nitrogen) that carries the molecules of the analyte through the heated column. The stationary phase is either a solid adsorbant, named gas-solid chromatography (GSC), or a liquid on an inert support, termed gas-liquid chromatography (GLC). The results are displayed in the form of a chromatogram, which is a reflection of the substance's affinity for the stationary phase; and is displayed as a plot between the peak area and the retention time (the time in which the specific compound "travels" through the column). The longer the retention time, the higher the substance's affinity for the stationary phase. Also, substances with long retention times often give broad peaks in the chromatogram. An example of a chromatogram peak is presented below (Fig. 1):

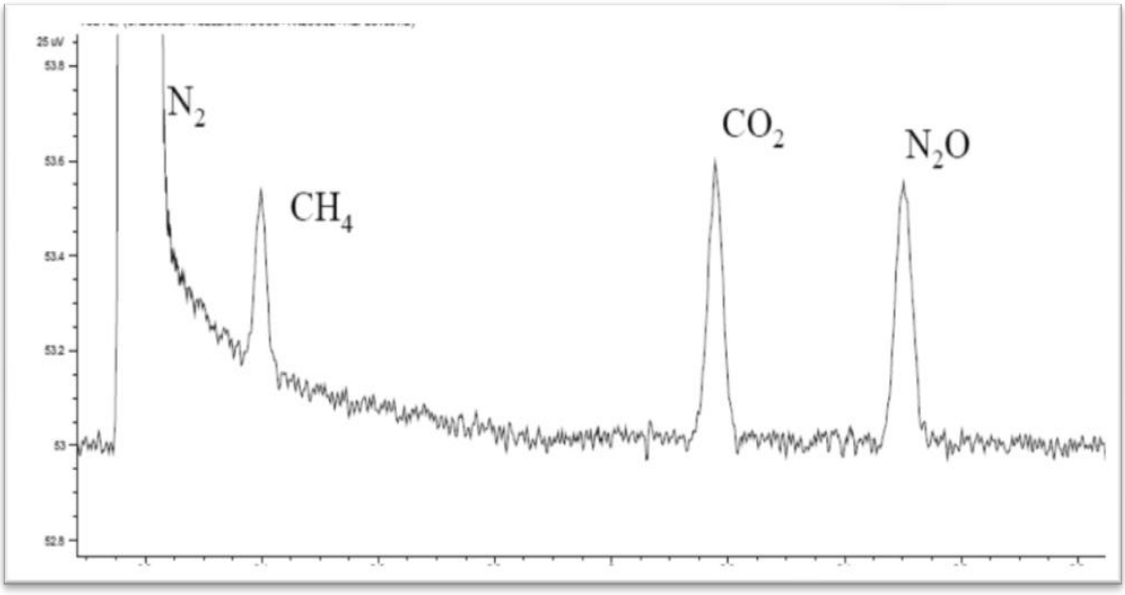


Figure 1. Example gas chromatogram performed on HP-PlotQ column. This column is employed in our experimentation.

3. Estimation of Membrane Performance

One of the most common approaches to estimate the membrane performance is the determination of the separation factor using the following approach (Eq. 1):

$$S_{ij} = \frac{\left(\frac{x_i}{x_j}\right)^P}{\left(\frac{x_i}{x_j}\right)^R} \quad \text{(Eq. 1)}$$

where:

S_{ij} - separation factor of component i over component j
x - molar fraction of gas compound
P - permeate
R - retentate

In order to determine mass transport through the membrane, flux (Eq. 2) and permeance (Eq. 3) have to be established:

$$J_i = \frac{x_i F^P}{A_m} \quad \text{(Eq. 2)}$$

where:

J_i - flux of permeating compound i ($mol.m^{-2}.s^{-1}$)
F^P - permeate flowrate ($mol.s^{-1}$)
A_m – effective membrane surface area (m^2)

$$\Pi_i = \frac{J_i}{\left(p_i^R - p_i^P\right)} \quad \text{(Eq. 3)}$$

where:

Π_i - permeance of compound i ($mol.Pa^{-1}.m^{-2}.s^{-1}$)
p_i - pressure of compound i (Pa)

To determine aforementioned parameters, estimation of mass balance across the membrane (*i.e.* composition of permeate and retentate stream) is a necessity (Eq. 4). This can be achieved as follows:

$$X_{in}F_{in} = X_{out}F_{out} \quad \text{(Eq. 4)}$$

where:

$$X_{in} = \begin{bmatrix} x_1^F & x_1^S \\ \vdots & \vdots \\ x_n^F & x_n^S \end{bmatrix}, \quad F_{in} = \begin{bmatrix} F^F \\ F^S \end{bmatrix} \qquad \text{(Eq. 5,6)}$$

$$X_{out} = \begin{bmatrix} x_1^R & x_1^P \\ \vdots & \vdots \\ x_n^R & x_n^P \end{bmatrix}, \quad F_{out} = \begin{bmatrix} F^R \\ F^P \end{bmatrix} \qquad \text{(Eq. 7,8)}$$

Experimental

1. Experimental Set-up

In this experiment the Wicke-Kallenbach method with on-line gas chromatography is employed; the experimental set-up is detailed below (Fig. 2). The Wicke-Kallenbach cell enables the separation of the feed and sweep stream via employment of the selective membrane. The feed stream comprises a mixture of the gases to be separated, whilst the sweep side employs an inert gas that enhances the extraction of the permeating species; the residue on the feed side of the membrane is called a retentate.

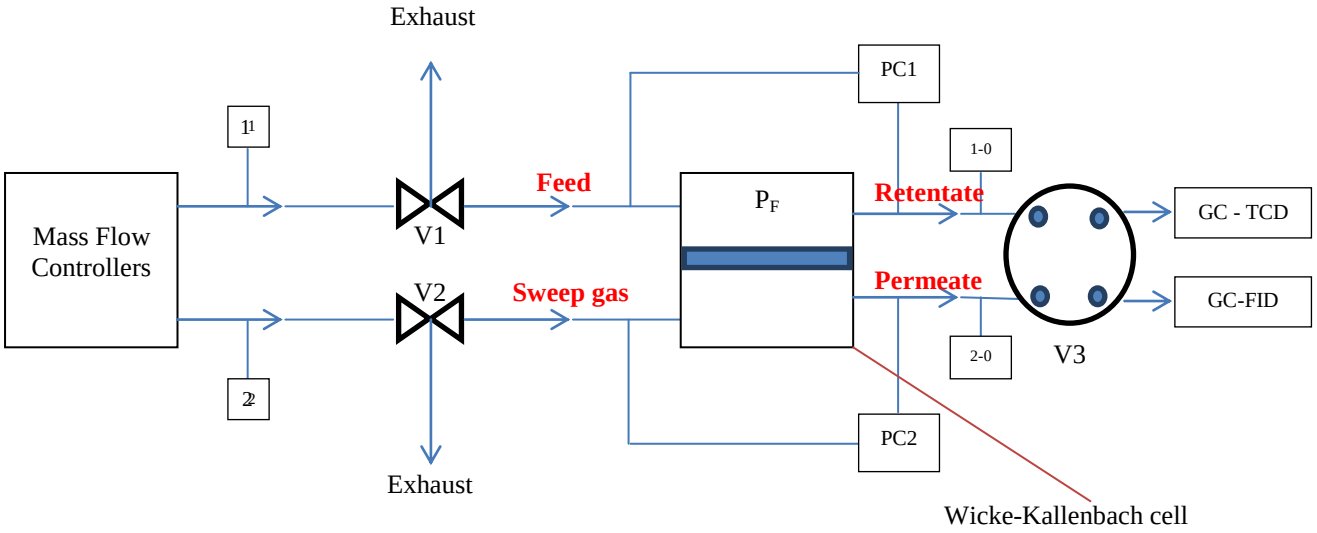


Figure 2. Experimental set-up.

where:

1 - feed pipe (F)
2 - sweep pipe (S)
1-0 - retentate pipe (R)
2-0 - permeate pipe (P)
PC - Pressure Controller

V - valve
GC - gas chromatograph

Note that for the purpose of this experiment, only GC-TCD (Gas Chromatograph with Thermal Conductivity Detector) is employed.

2. Experimentation

The specific steps to conduct this experiment are detailed below:

1st Step: Calibration of Gas Chromatograph

Prior to the calibration of gas chromatograph, all mass flow controllers (MFCs) to be used require calibration. Once this task is completed, GC should be calibrated as follows:

1) Set a composition with MFCs (ideal gas relation: volumetric fractions are equal to molar fractions).
2) Run GC and note pressure in sample loop before gas injection.
3) Identify the peaks and determine the peak areas.
4) Derive molar quantity in the sample loop from ideal gas relation (V=250 mL)
5) Derive molar quantity of each gas from previous step.
6) Attribute each peak area to corresponding gas molar quantity.
7) Repeat for different compositions.

2nd Step: Mounting Wicke-Kallenbach cell

Place a membrane in an adapted joint and ensure that it is sealed properly as any gas leak will result in the false experimental data. Afterwards, connect both 1 and 1-0 pipes to the feed side of the cell (facing the membrane); and pipes 2 and 2-0 to the other side. Send the sweep gas through.

3rd Step: Feed and Sweep settings

To ensure the accuracy of the obtained data, a precise determination of the composition of the gas that enters the system is crucial; this can be ascertain using MFCs. Assuming the gaseous mixture to be separated behaves as an ideal gas, volumetric ratios can be presumed to be equal to the molar ratios.

For the purpose of this experiment helium is utilised as a sweep gas with a constant flow rate kept at 10 $mL.min^{-1}$. Pressure on both sides of the membrane, as well as the inlet gas temperature, can be varied in order to optimise separating conditions. Cernobyl software is used to set process parameters (for more details see *Appendix A*).

Before starting experimentation, the gas flowrates have to be validated. This can be achieved as follows:

1) Set the desired value using Cernobyl programme.
2) Switch the corresponding valve to the position A in such way that the gas exits through exhaust.
3) Measure the exhaust gas flow rate using the bubble flow meter.
4) Once the verification of the flow of all the gases is completed, switch the valve to the position B.

Please note that the above requires the treatment of one gas at a time. The procedure should be repeated for all gases present in the mixture.

5^{4h} Step: Data Acquisition

Once the feed composition and no leak in the system are ensured, experimentation can be undertaken. For the purpose of this experiment, Chrom-Card programme will be employed (however note that it can also be set up automatically via Cernobyl software).

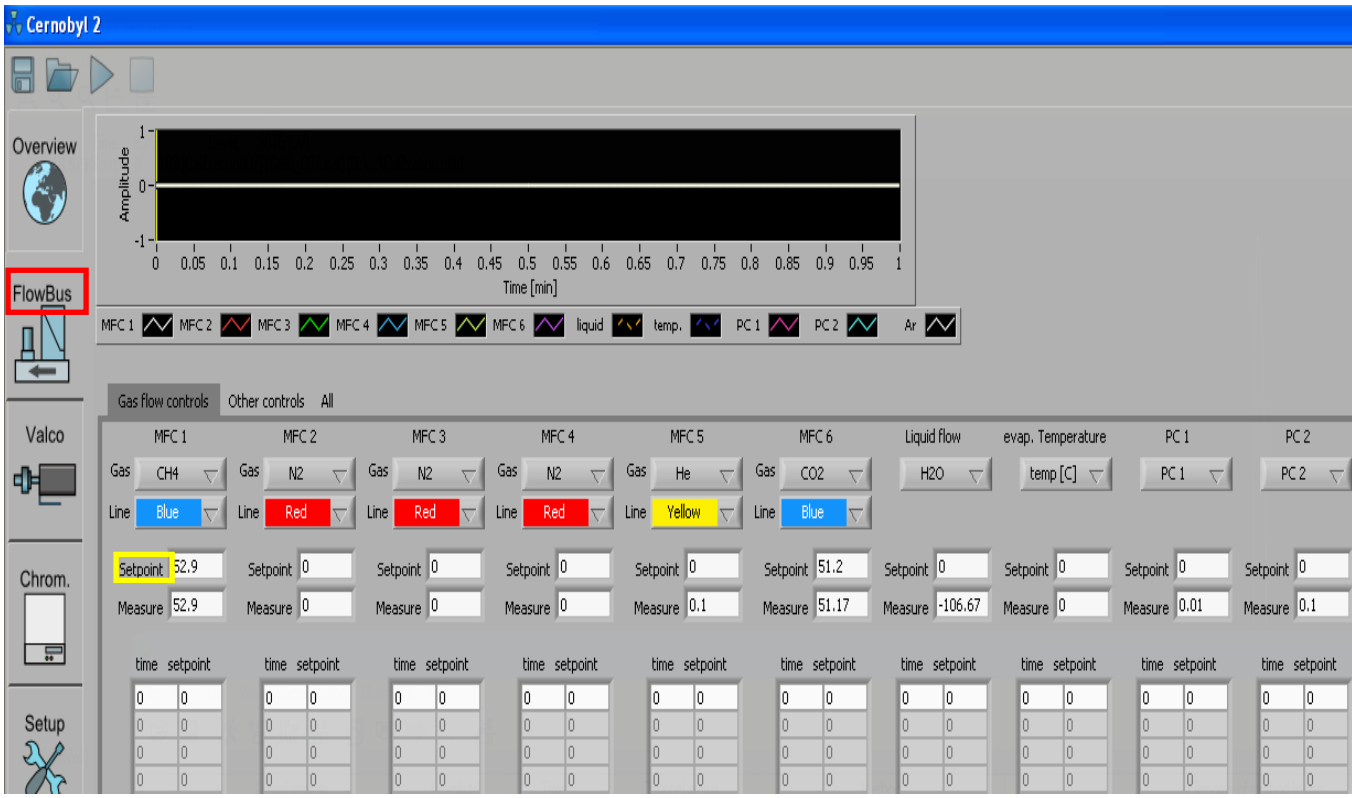
5th Step: Results Exploitation

The concentrations of the solutes are determined from the peak areas that are automatically calculated by the Chrom-Card software. If the chromatograph is not running, the exiting gas mixture is going through the sample loop (this is valid for any gas side to be chosen). Once the gas chromatograph is set up and running, the sample in the loop is injected into the column and the data acquisition begins.

The pressure in the sample loop at the time of injection gives the molar quantity of the analysed gas stream (according to the Ideal Gas Law). The molar quantities of the compounds present in the sample loop can be obtained from the chromatograms. The ratio between the two above gives the composition in the sample loop, and by extent, the composition of the mixture exiting the system.

APPENDIX #1: Cernobyl Interface Tutorial

Cernobyl is used to set flowrates and pressure/temperature parameters for the measurements:



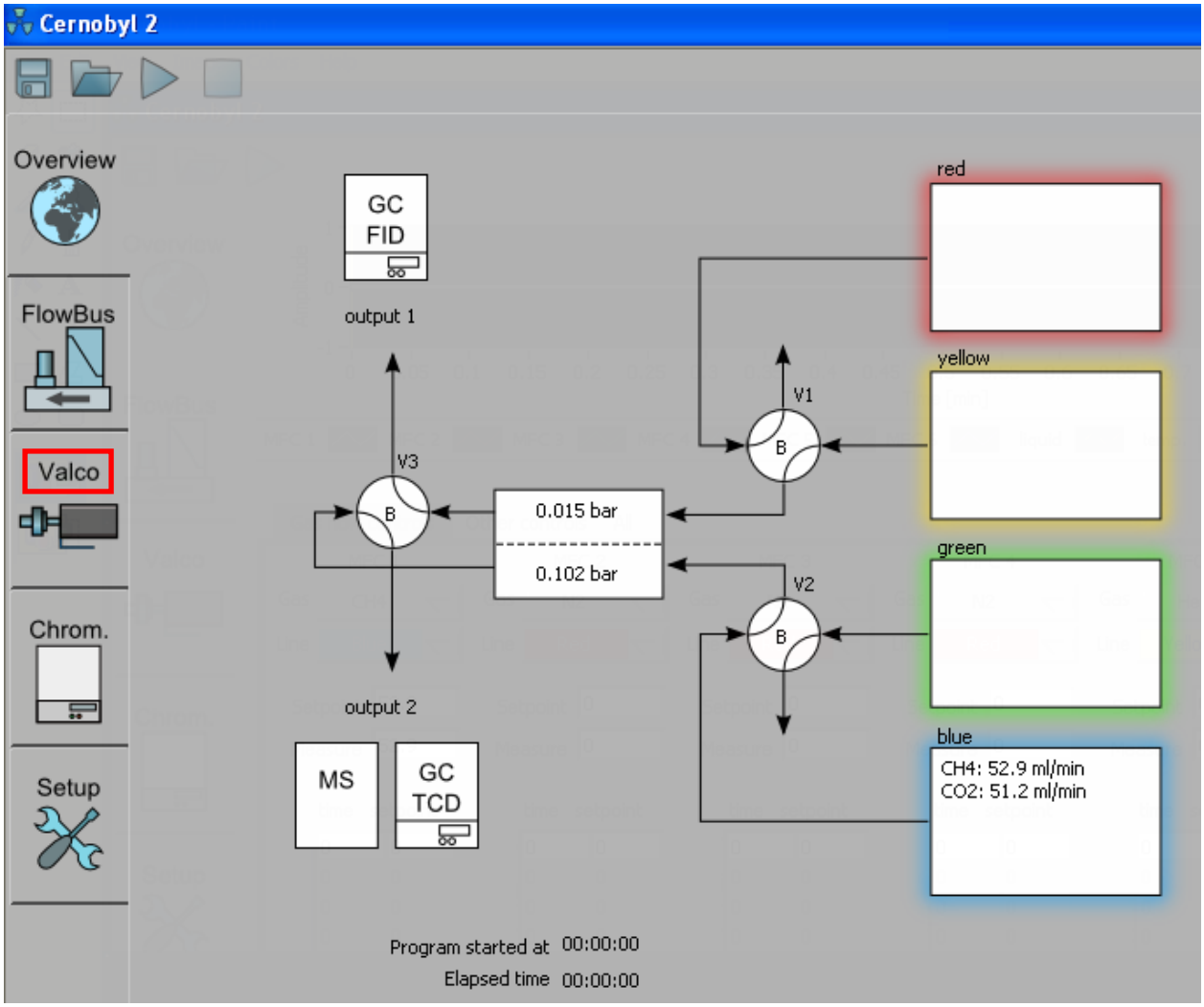
- Once Cernobyl launched, first click on FlowBu tab.

- MC1, MFC2 … represent the Mass Flow Controllers, PC1 and PC2 the Pressure Controllers. Change Gas Label to use the correct calibration of the MFC. At the contrary, changing the color of the line will NOT change the line; it is just a reminder of which gas goes where. This has to be set using the valves on the panel of the MFCs.

- Set the values of flowrates and pressures using Setpoint. 'Measure' labels correspond to the measured values given by the apparatus.

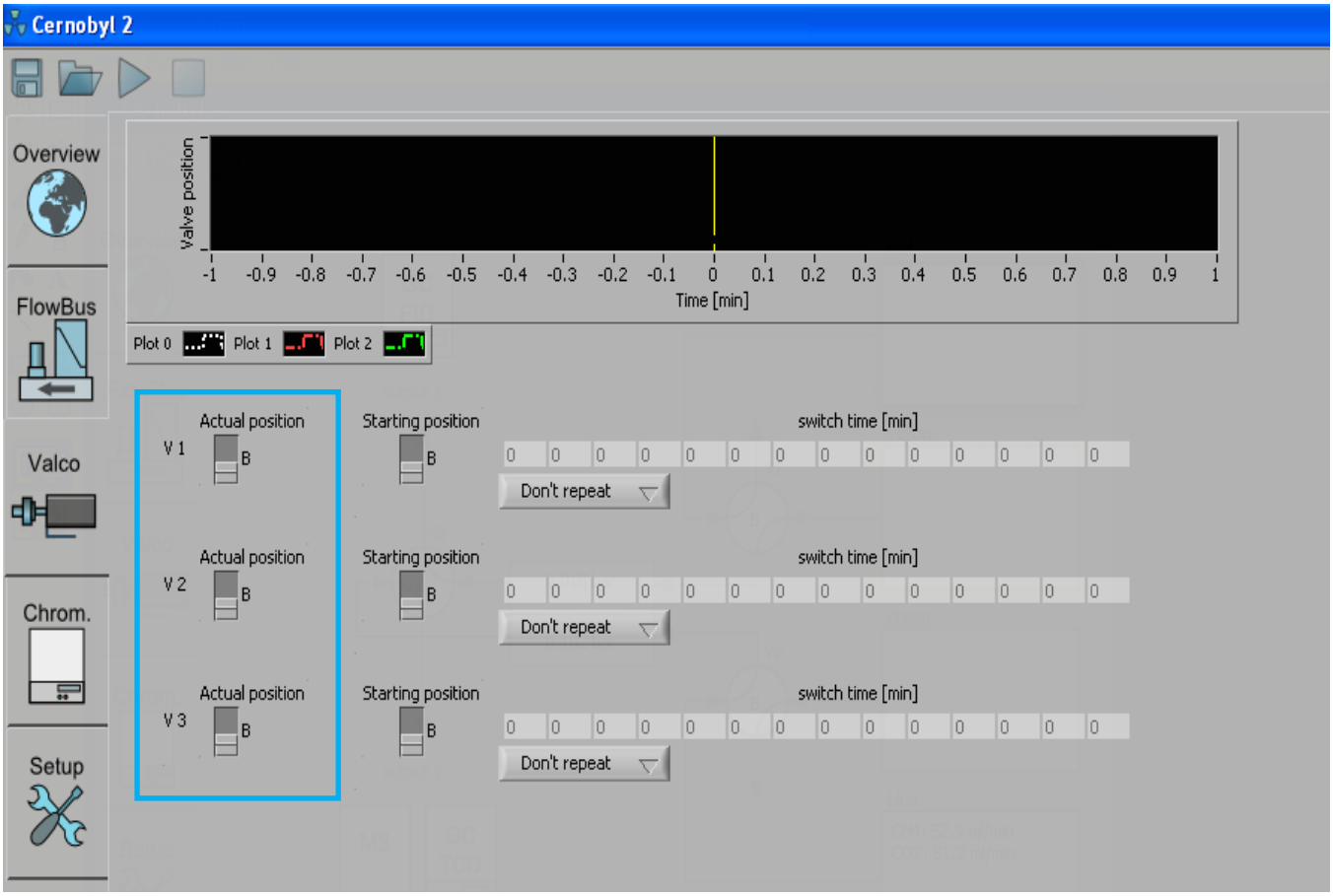
- Time and Setpoint tables are only used when measurements are run automatically.

Once the values set, use the 'Overview' tab:



This shows where the gas is going, depending on the positions of the valves. **/!\ This overview is accurate only if the colors of the lines in Cernobyl match with the colors of the pipes used in the panel.**

To change an orientation of a pipe, valves positions have to be switched. To do so, click on Valco tab



- Valves have 2 different positions: A and B. Switch them from one position to another by clicking on the corresponding valve button. A noise can be heard when a valve has changed position successfully.
- Use Actual only, what remains is used for automatic measurements.

Before any measurement, make sure everything is OK, by checking the 'Overview' tab.