Preparation of Gas Mixtures

April 2022

Multicomponent mixtures ranging in concentration from PPM to nearly 100% are common. A typical gas mixture is a two component one, with the balance gas being an inert or flammable gas

For safety and stability reasons, gases nonreactive with each other are mixed. The following are combinations that are known to react and with few exceptions should be avoided:

Fuel - Oxidizer ⇨ $N_2O + SiH_4$

Acid - Base ⇨ $HCl + NH_3$

Fuel Oxidizer mixtures can be made under strict guidelines, see Explosive Gas Mixtures

Testing has also shown others that react such as

$SiH_4 + SF_6$ ⇨ SiH_4 + R-13

Hazard Classifications of mixtures are:

1. Toxicity based on ISO 10298 - Gas cylinders — Gases and gas mixtures — Determination of toxicity for the selection of cylinder valve outlets
2. Flammability based on ISO 10156 - Gas cylinders -- Gases and gas mixtures -- Determination of fire potential and oxidizing ability for the selection of cylinder valve outlets
3. Oxidizer - Oxygen >23.5% based on ISO 10156 - Gas cylinders -- Gases and gas mixtures -- Determination of fire potential and oxidizing ability for the selection of cylinder valve outlets
4. Corrosivity – based on ISO 13338 - Gas cylinders — Gases and gas mixtures — Determination of corrosiveness for the selection of cylinder valve outlet

These are recognized by the UN Globally Harmonized System, Transport of Dangerous Goods, International Fire Code and National Fire Protection Association.

For liquefied gas blends, the maximum mixture pressure is based on component partial pressures plus safety factors to ensure that the liquid component does not liquefy due to cold temperatures during transportation or storage. This is accomplished, in most cases, by reducing the final pressure of the mixture so as it is below its saturation pressure. In certain other specific binary mixtures, e.g. N_2O/O_2 (Entonox) the Poynting Effect is used to determine the final pressure.

For example, Arsine which has a vapor pressure of 205 psig at 70^oF (21^oC), the mixtures can only be made to the following top pressures

15% Arsine - 1010 PSIG
10% Arsine - 1525 PSIG
5% Arsine - 1800 PSIG

Once it has liquefied, it will not remix even when warmed unless it is mechanical rolled

Preparation

Pressure Gauge

Making gas mixtures using a pressure gauge is very inaccurate due to poor precision of pressure gauges at high pressures. In addition, gases do not behave ideally. Affects from

1. Temperature
2. Compressibility, and
3. Synergistic affects between gases

all contribute to the overall inaccuracy of the final mixture.

Silane for example

Gravimetric

The most accurate method of preparing a gas mixture is to prepare it on a very sensitive scale (Gravimetric), weighing each gas as it is added

A Voland scale is a triple beam balance which is enclosed a cabinet to reduce the influence of air movement. It has a sensitivity of 10 mg for a 49 liter carbon steel cylinder.

If weights used are directly traceable to international standards a traceable gas standard can be made for calibration.

Government regulations require calibration standards for pollution measurements to be traceable.

Accuracy of the gas mixture can be affected by

1. Scale precision
2. Scale calibration
3. Pigtail stress from pressure
4. Amount of gas added (smaller the amount the less accuracy)
5. For low ppm mixtures the reaction of the cylinder walls or moisture contamination can degrade the quality of the mix.
6. Decomposition (e.g. Diborane) can reduce its concentration over time.

For example

A 1% PH_3 balance H_2 mixture in a 49 liter cylinder at 2,400 psig of pressure requires the addition of 100 gms of PH3 and 589 gms of H_2.

1. If a scale has an accuracy of + 5 gms the mixture concentration can be 0.93-1.05%
2. If a scale has an accuracy of + 1 gms the mixture concentration can be 0.98-1.01%
3. If a scale has an accuracy of + 0.1 gms the mixture concentration can be 0.98-1.01%

The smaller the amount of the PH_3 addition, the worse the accuracy will be.

After all of the additions, the gases must be homogenized using one or more of the following techniques.

1. Heat lamp at bottom of cylinder (CAUTION – Do not allow cylinder to exceed 130^{o}F)
2. Lay cylinder horizontal overnight
3. A roller that rolls clockwise and then counterclock wise for an hour in one minute increments.
4. Mixing tube inside cylinder.

Adding components in increasing order of density, where possible.

Preparing mixtures in more than one cylinder can be a challenge due to system design causing unequal flow conditions. The most common systems are:

1. Linear manifold
2. Spider manifold
3. Branched manifold
4. Dynamic Blending

Minor component is first put into all cylinders.

Balance gas is then introduced.

Variance between cylinders can occur due to:

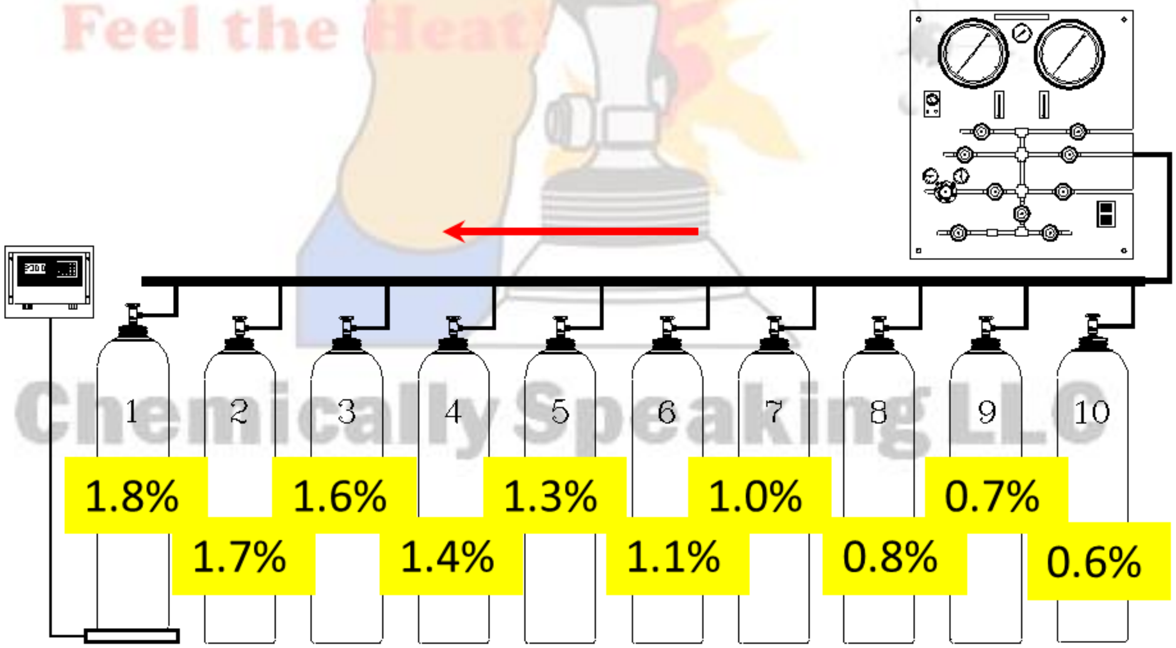
1. Valve Problem
2. Operator Technique
3. Not Rolling
4. System design

One cylinder in the batch is on a scale and controls the additions. After the addition of the minor component the cylinders are allowed to equalize in pressure. The addition of the balance gas then proceeds.

Linear Manifold

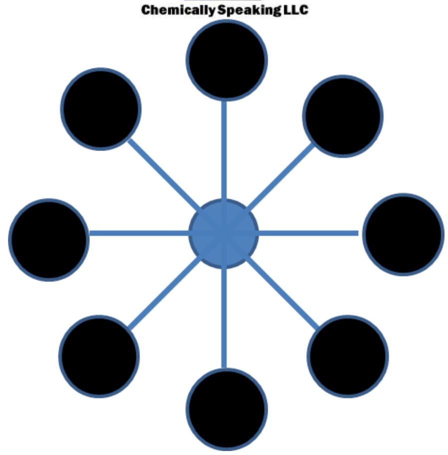
A linear manifold takes considerably more time to put in the balance gas due to having to add it slowly. so as not to suck out the gas and put it into the other cylinders

The balance gas would have a Venturi effect at high flow rates and suck the minor component out of the initial cylinders transferring it into the latter cylinders on the manifold. For example, a 1% Phosphine mixture would have a higher concentration in cylinder #1 while cylinder #10 would be lower.



Spider manifold

A circular system with cylinders equal distance around the manifold. The piping length to each cylinder is the same so flow is the same.

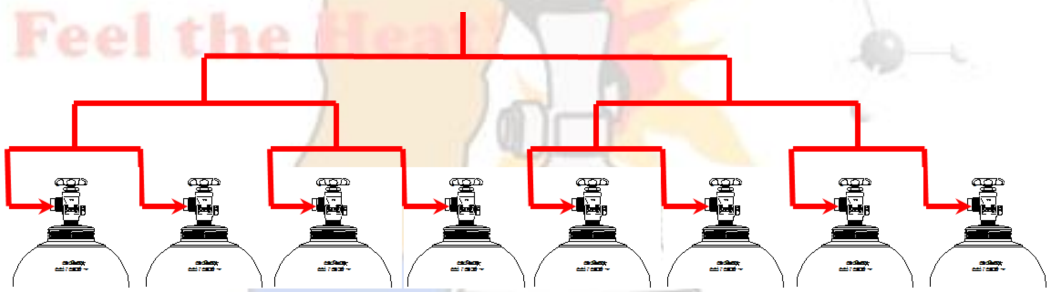


If a cylinder valve is not fully open or has a Cv difference, it can cause an inaccurate mixture in that cylinder.

Branched Manifold

The piping length to each cylinder is the same so flow is the same

If cylinder valve is not fully open or has a Cv difference, it can cause an inaccurate mixture in that cylinder.



Dynamic Blending

Continuously blend both gases using MFC's and compress it into cylinders. Some systems have an on line analyzer. An expensive diaphragm compressor must be used to pressurize the mixture into the cylinders. This technique is not as accurate as scale methods.

Analysis

Individual cylinders of mixtures made gravimetrically with good weight numbers do not require analysis for concentration determination. The concentration values will be calculated based on the weights values.

Mixture cylinders made in a batch with a scale are analyzed after rolling to determine variability. A batch analysis is where a few cylinders are analyzed and if the variance is within the acceptable range, the average of the concentrations is assigned to the batch. (Batch Analysis)

Individual analysis is where each cylinder is assigned its own concentrations from the analytical data.

Cylinders made as a batch are analyzed for concentration using mixtures with known concentrations. Typically using a mixture made gravimetrically. At a minimum, the calibration gas mixtures must be of a concentration higher and lower than the mixture being analyzed and as close as possible to the concentration. This will minimize errors due to nonlinearity.

Calibration gas mixtures must be run periodically throughout the shift to determine variability due to instrument drift.

Eugene Ngai