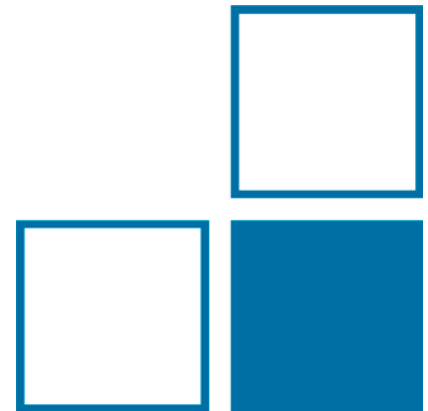


Preparation of wet test gases

Henry's Law and its application in
“saturation type”- test gas sources

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Properties of a wet test gas

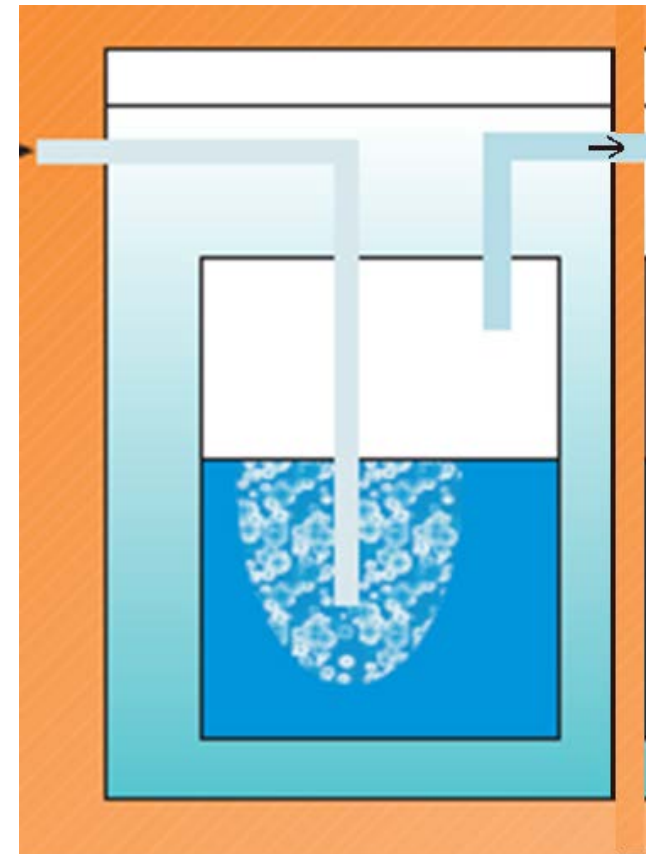
According to OIML R 126, a test gas source should be able to deliver gas with:

	<i>Basic properties</i>	<i>Advanced properties</i>
Composition	air, water, ethanol	Carbon dioxide
Ethanol concentration	0 mg/L... 2 mg/L	up to 3 mg/L
Temperature:	34 °C ± 0,3 °C	30 °C ... 40 °C
Volume flow rate	6 L/min ... 20 L/min	up to 36 L/min
Relative humidity	> 95 %	
Pressure	No requirements	
Relative uncertainty	< 1,6 %	
Realisation	transient gas flow	

Principle of an easy and wide-spread set-up:

Pressurized air is led through a water-ethanol-solution:

- The gas bubbles take up ethanol and water from the solution till saturation
- The generated concentration depends only on the temperature and the ethanol concentration in the liquid phase
- This saturation or equilibrium between the liquid and the gaseous phase can be calculated with Henrys Law



Henry's law describes the solubility of gases in water, which is proportional to its concentration in the gas phase

$$H^{cc} = \frac{c_{aqueous}}{c_{gas}}$$

- Equilibrium of concentration in both phases
- This is applicable not only for gases but for volatile water-soluble substances as well
- Each substance builds up its own equilibrium, depending on boiling point, solubility in water and the actual temperature
- this volatility can be expressed as K (partition coefficient)

$$K^{cc} = \frac{c_{gas}}{c_{aqueous}} = \frac{1}{H^{cc}}$$

Henry's law for ethanol in water/ air

Considering the temperature influence, Henrys law can be described as:

$$c_{gas} = K_0 * c_{solution} * e^{(K_1 * t)}$$

with: K_0 : partition coefficient of a substance (dimensionless)
 K_1 : temperature dependency coefficient of the substance
 t : temperature of the solution/ system in °Celsius

For ethanol in an aqueous solution, the following formula, the so-called Dubowski-equation can be used:

$$c_{gas} = 0,04145 * 10^{-3} * c_{solution} * e^{(0.06583 * t)}$$

with: c_{gas} : concentration of ethanol in the gas phase in g/L
 $0.04145 * 10^{-3}$: partition coefficient K_0 for ethanol (dimensionless)
 $c_{solution}$: concentration of ethanol in the solution in g/L
 0.06583 : temperature dependency coefficient K_1
 t : temperature of the solution in °Celsius

For 34°C as temperature for the solution and the gas, it can be reduced to:

$$c_{gas} = 0,38866 * 10^{-3} * c_{solution}$$

The Dubowski-equation is used in many countries and is also recommended by OIML R126, but:

- The partition coefficient is only an empirical value from literature, without any estimation of uncertainty
- Some countries like USA use a slightly different partition ratio (Hargers formula). For 34°C it is:

$$c_{gas} = 0,393 * 10^{-3} * c_{solution}$$

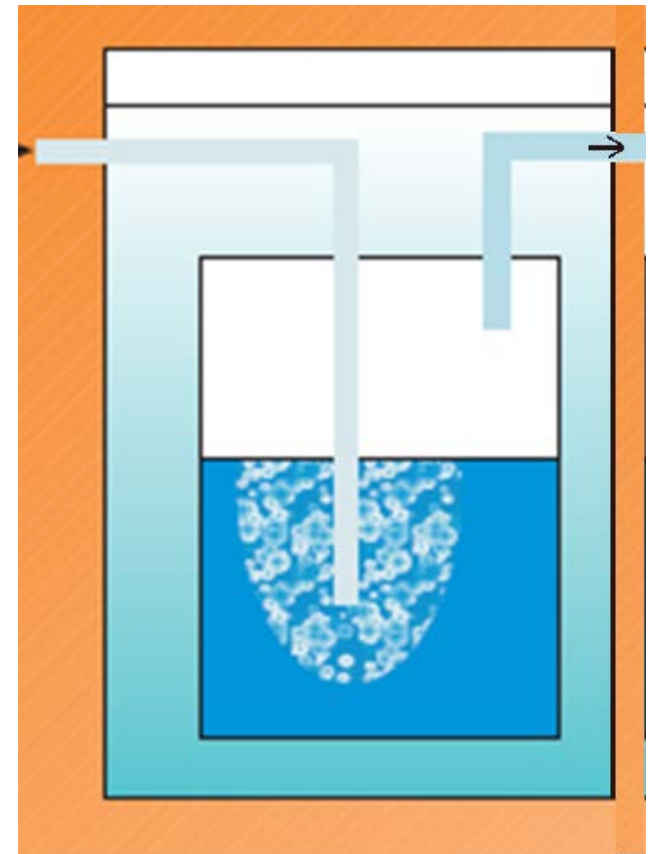
For an concentration of the solution of 1,0292 g/L, this leads to:

- Dubowski: $c_{gas} = 0,38866 * 10^{-3} * 1,0292 = 0,0004 \text{ g/L} = 0,400 \text{ mg/L}$
- Harger: $c_{gas} = 0,393 * 10^{-3} * 1,0292 = 0,000404 \text{ g/L} = 0,404 \text{ mg/L}$

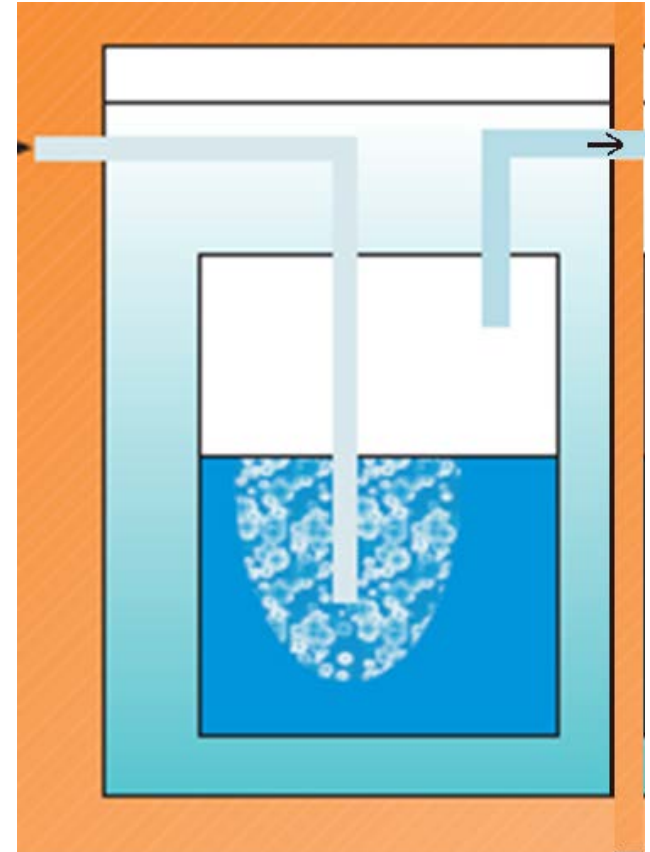
→ systematic difference of 1 % !

→ Henry's law was developed for static equilibria and systems
→ It will apply also on dynamic equilibria in closed systems:

- When air is lead through a solution, the air will be enriched with ethanol and a momentary equilibrium will be established
- Simplest set-up:
One gas-washing bottle with an internal or external heating system

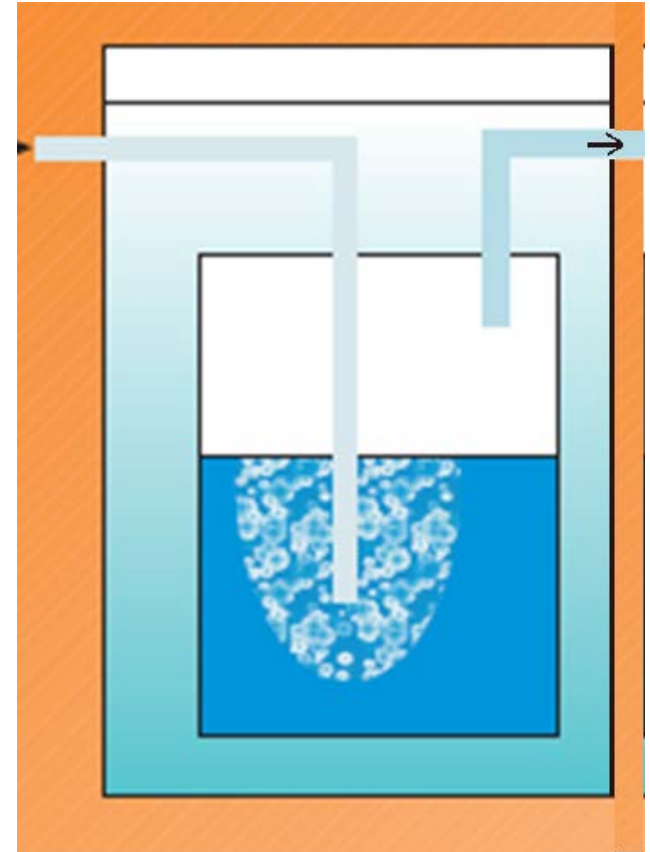


- When led through a sintered glass filter (frit), the air passes the liquid in myriads of little bubbles
- Within each bubble, it is assumed that the equilibrium between the gas and the liquid phase is formed instantaneous. This goes both for water as for ethanol
- As a result, the concentration of gas reservoir is in equilibrium with the concentration of the liquid phase
- When more gas is lead into the flask, the equilibrated air reservoir will leave the bottle and new air can interact with the liquid.



Problems of 1-flask-set-ups:

- The ethanol in the liquid phase will be washed out by the flow of air
- The equilibrium concentration will drop constantly because of the decreasing ethanol concentration of the solution
- The evaporation of water and of ethanol consumes much energy, which will be taken out of the solution and the temperature in the flask will decrease
- Heating system is necessary for the compensation of the energy loss and the temperature stabilization

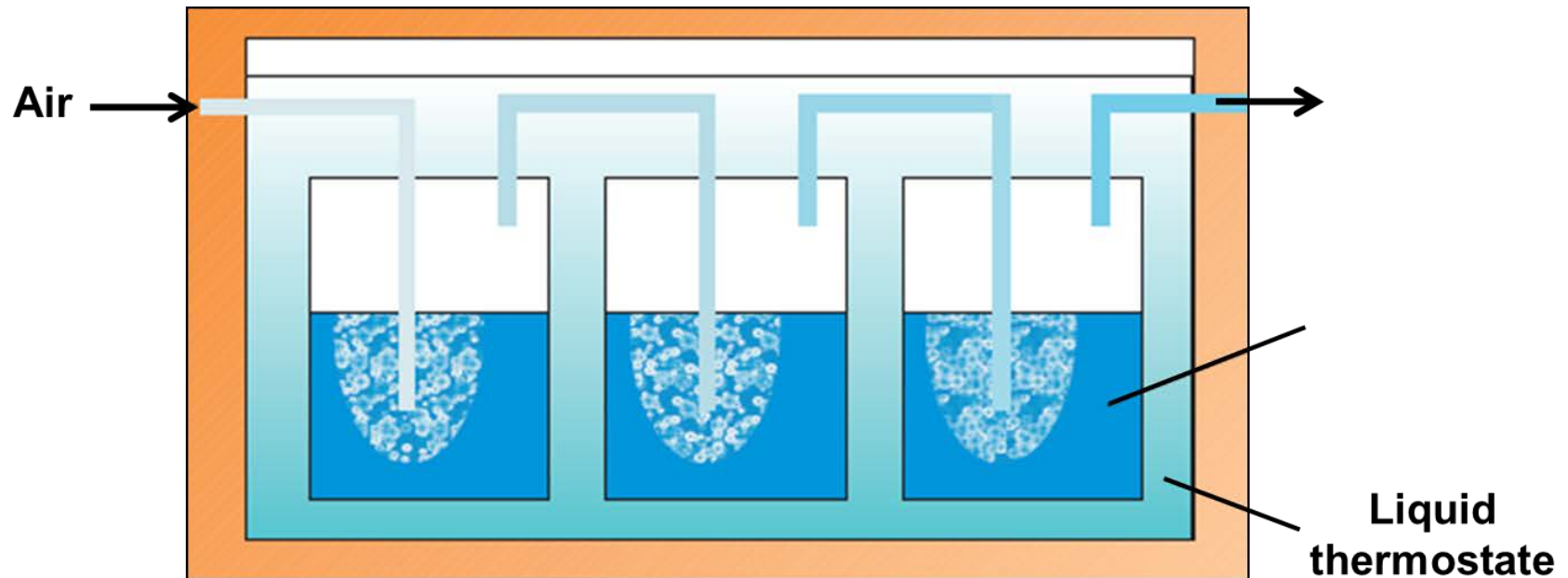


Application to dynamic systems (4)

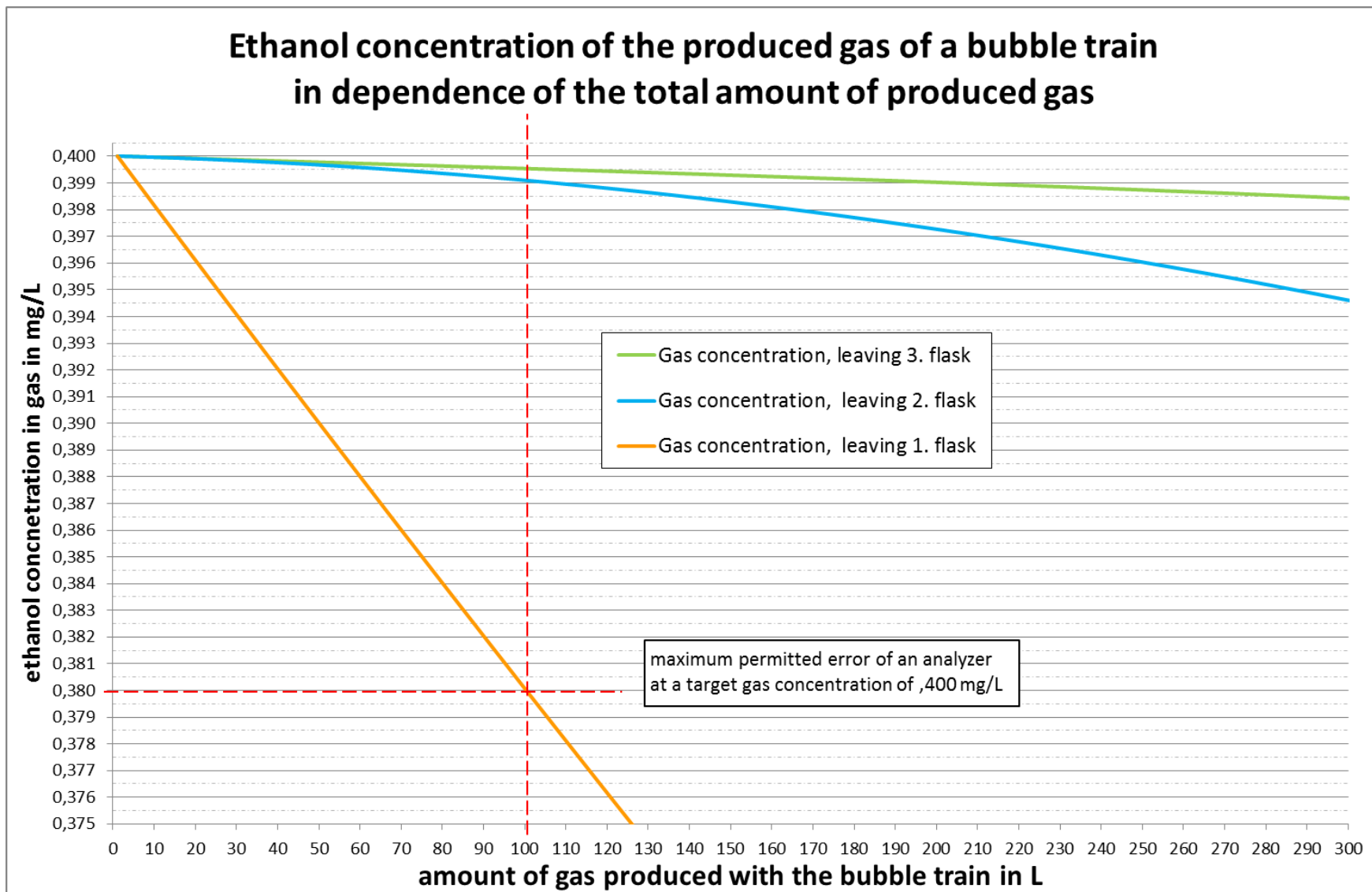
To encounter the constant decrease of the ethanol concentration and the instable temperature, two or three flasks can be coupled to a series which will be placed in a thermostatic bath.

Advantages:

- The air which enters the following flasks will be pre-saturated, so that the second and third flask only have to supply the missing amount for an equilibrium
- In the third flask, which is crucial for the final gas concentration, the temperature can be considered as stable, since only little evaporation takes places and the thermostat will ensure a stable ambiance for both liquid and test gas.



Bubble train in use



Regarding a 3-flask bubble train:

Advantages	Disadvantages
Easy to handle	Warm-up time of at least 60 min
Stable gas concentration up to 120 L of produced test gas ($< 0,125$ % decrease)	For change of concentration, a different solution has to be put into the flasks
Only two parameter have to be controlled (temperature and concentration of the solution)	The influence of the pressure which builds up inside the flasks is not considered in the Dubowski-equation
Certified reference material (water-ethanol-solution) for traceability	There is no proof if the saturation to equilibrium still works with higher flows (> 20 L/min)
	Not easily transportable

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For the uncertainty of the produced gas concentration with a 3-flask-bubble train the following quantities have to be taken at least into account:

1) Quantities deriving from Henrys law:

Quantity	Remarks/ considerations
Temperature of the solution/ gas	Temperature measurement in the 3. flask needed, value of contribution to uncertainty depends on the quality and resolution of the temperature sensor
Ethanol concentration of used solution	Use of CRMs with specified uncertainty of the concentration
K_0 partition coefficient for ethanol	Only empirical values without Uncertainty values available .
K_1 temperature dependency coefficient for ethanol	→ Considered as a conventional approach with no uncertainties for the coefficients. But: Values of Dubowski and Harger already differ by 1 %!

2) Quantities deriving from the use:

Quantity	Remarks/ considerations
Temperature stability in the 3. flask within one measurement	Observation data of the temperature alteration within one measurement/ one portion of test gas
Condensation of liquid (water + ethanol) out of the test gas	Only occurs if the temperature of the gas tubing leading out of the set-up is below the temperature of the liquid/ flask. If no condensation is monitored, this influence can be considered as neglectable.
Difference of gas pressure in the 3. flask and in the measuring instrument	Observation data of pressure at the respective points , calculation of the change of concentration caused by the change of volume

- There may be more quantities influencing the actual test gas concentration, here only the most important one were shown.
- When considering not only one portion of the gas, but a test gas series, additional quantities for the stability of the temperature and the decrease of the ethanol concentration in the solution
- No overall solution for an uncertainty estimation, each test set-up has to be considered separately, taking into account the actual terms and details
- The influence of each quantity has to be expressed in the unit of the test gas concentration to estimate the effect on it and to calculate the Uncertainty

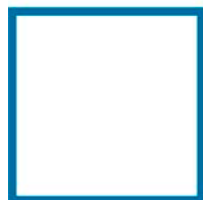
The model equation is based on the Henry equation plus the effects of loss due to condensation and volume change:

$$c_{gas} = K_0 * c_{solution} * e^{(K_1 * t)} - \Delta_{c_{gas} \text{ condensation}} - \Delta_{c_{gas} \text{ volumechange}}$$

$$\Delta_{c_{gas} \text{ volumechange}} = \left(1 - \frac{p_{instrument}}{p_{flask}}\right) * (K_0 * c_{solution} * e^{(K_1 * t)})$$

Now, an uncertainty budget has to be estimated, considering for each quantity the value, the type and distribution and its limits or uncertainties.

→ This is only a model for demonstration. For sure, other ways for setting up the equation will exist!



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