Effective Volumetric Factor for Inhomogeneous Temperature in Volumetric Measurements of Gas Absorption and Desorption

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Abstract

Accounting of effective volumetric factor for the measurement at inhomogeneous temperature allows to simplify the measurement process avoiding a pre-calibration with a noble gas. The volumetric correction in form of the volumetric factor is calculated analytically by modeling of the temperature profile in the volumetric apparatus, and provides a quite agreement with the measured results. The calculation can be applied for each volumetric measurement with an inhomogeneous temperature distribution.

Keywords: Sievert’s apparatus, adsorption, desorption, volumetric, temperature inhomogeneity.

1 Introduction

The measurements of the gas absorption and desorption are mostly performed in a volumetric equipment. A precise control of the gas amount at

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the inhomogeneous temperature distribution is an essential issue for correct evaluation of experimental data.

Volumetric Sievert's apparatuses are widely used for experiments on gas absorption and desorption. They are relatively low cost equipment compared to more expensive gravimetric equipment.

A volumetric apparatus like represented in [1] consists conventionally of a volumetric pool and a sample holder with the sorption material. During the adsorption/desorption, the sample is kept at the certain temperature. This temperature is not the same, as in the volumetric pool.

In the exceptional case, when the temperature $T$ of the sorption gas is homogeneous distributed within the measurement setup, the normal state equation is used.

$$ \nu = \frac{p}{R} \left( \frac{V}{T} \right), $$

(1)

to obtain a molar amount $\nu$ of the gas at the pressure $p$, $V$-total volume, $R$-molar gas constant.

If the gas is stored in several volumes $V_1, V_2, ..., V_n$ at different temperatures $T_1, T_2, ..., T_n$, the total molar amount is calculated as:

$$ \nu = \frac{p}{R} \{V/T\}; \text{ where } \{V/T\} = \frac{V_1}{T_1} + \frac{V_2}{T_2} + ... + \frac{V_n}{T_n}, $$

(2)

and is defined as the effective volumetric factor, that should be used instead of the ratio $V/T$ in (1). In case, when the sample holder is heated/cooled, the gas temperature is distributed inhomogeneous. To establish the resulting volumetric factor $V/T$, some empirical ways are possible. One can use a non-adsorptive gas before the main measurement starts. In our measurements, the volumetric setup with the static inhomogeneous temperature distribution has been filled with helium. After two measurements of pressure in states with closed and open sample holder respectively, the equipment has been completely evacuated and the adsorptive measurement gas (hydrogen) was introduced to the system.

This simple and convenient method has certain shortcomings. There are some of these:

1. The pre-measurement including the following exhausting is significantly time consuming, compared to the duration of the main measurement.

2. This procedure could not be applied micro- and nano-porous materials, due to possible adsorption in porosities also for helium gas.

3. The method is not applied for the measurements with variable temperature.
V - the volume of the holder with the sample and hot gas in the thermostat at $T_0$

$V_p$ - volume of the pipe channel containing the gas with the descendent temperature from $T_{ch}$ down to $T_c$

$V_s$ - the system volume behind the ventil, with the cold gas of temperature $T_c$

$T_1, T_2, T_{ch}$ the temperature measured in control points.

$T_c, T_0$ are set by the experiment conditions.

Figure 1: Structural scheme of the volumetric apparatus.

In the present work we have modelled the temperature profile in the volumetric apparatus with respect to the temperature measured in several points. The expected volumetric factor for this temperature distribution is calculated analytically. The experimental verification shows an exact agreement with the measured result.

## 2 Volumetric Principle

The calculations and verification were performed for the volumetric apparatus BELSORP-HP, BEL Inc.Japan. The construction and principle of measurement is briefly described, as follows: Before the main measurement, the active sorption volume (‘dead volume’) $V_d = V_p + V_H$ should be determined using the helium gas. The proper volume of the sample holder $V_H$ is calculated from its geometry. The molar amount of adsorbed/desorbed gas is evaluated from the difference of pressures in initial $n$ and final $n+1$ states:

$$\nu_{ads/des}^{n \rightarrow n+1} = \frac{(p_n - p_{n+1})\{V/T\}}{R}$$ (3)

The initial state $n$ corresponds to closed connection between the holder
$V_p, V_H$ and the volumetric pool $V_s$, whereat the pressure in the $V_H$, and the
gas in $V_H + V_p$ remains at the pressure of the previous step $p_{n-1}$.

Each sorption step starts by opening of this connection. The pressure
inside the setup (chamber) balances and the sorption begins. The current
step is stopped in two cases, namely:

1) if no alteration of pressure is observed, or otherwise

2) after the certain time.

The pressure reached in this step corresponds to the final state $p_{n+1}$. The
measurement principle and procedure is described in details elsewhere [2].

3 Accounting of the Temperature Inhomogeneity

3.1 Basic assumptions on the Temperature Distribution

The sample holder is typically designed as a pipe. All other gas connectors
and conductors of the volumetric apparatus are pipes as well.

Hence, the following suggestion is commonly applied: the inhomogeneous
temperature distribution is modelled for gas containing parts with transla-
tional symmetry. Let $z$ be a length coordinate along a pipe. The loss rate
of the heat energy [J/s] in the surrounding air (thermic bath) of the tem-
perature $\bar{T}$ with an empirical heat transport coefficient $\kappa$ per segment $\Delta \sigma$ of
surface is supposed to be:

$$\Delta Q = \kappa [T(z) - \bar{T}] \Delta \sigma, \quad (4)$$

and the infinitesimal decrease of temperature at the point $z$ caused thereby
is:

$$\Delta T(z) = -\lambda C \Delta Q = -\lambda C \kappa [T(z) - \bar{T}] \Delta \sigma \quad (5)$$

Assuming a translational symmetry of the gas container (pipe), $\Delta \sigma = S \Delta z$, $S$- perimeter of the cross-section, $\Delta z$- infinitesimal part of length, and
changing to differential values, one obtains:

$$dT(z) = -\lambda SC \kappa [T(z) - \bar{T}] dz := -\tau [T(z) - \bar{T}] dz. \quad (6)$$
An immediate integration with the initial condition \( T(z)|_{z=z_0} = T_0 \) provides an exponential decrease of the temperature along the pipe container/channel, characterized by its cumulative parameter \( \tau \)

\[
T(z) = (T_0 - \bar{T})e^{-\tau(z-z_0)} + \bar{T},
\]

(7)

the simple "shifted exponential descent", that will be used further as an ansatz of the temperature distribution along the sample holder (also treated as a gas temperature).

The parameters \( \tau, z_0 \) of this distribution are provided by measurements of \( T \) in two points \( z_1, z_2 = 2z_1 \) to be

\[
\tau = \frac{1}{z_1 - z_0} \ln \frac{T_0 - \bar{T}}{T_1 - \bar{T}} = \frac{1}{2z_1 - z_0} \ln \frac{T_0 - \bar{T}}{T_2 - \bar{T}},
\]

(8)

\[
z_0 = z_1 \left[ 1 - \frac{1}{\ln \frac{T_0 - \bar{T}}{T_2 - \bar{T}} / \ln \frac{T_0 - \bar{T}}{T_1 - \bar{T}} - 1} \right]
\]

(9)

### 3.2 Modelling of the Temperature Profile and the Effective Volumetric Factor

The total molar content \( \nu \) of the gas in the system related to the common pressure \( p \):

\[
\frac{\nu}{p} R = \{V/T\}, \text{ where the effective ratio } \{V/T\}
\]

(10)

is composed of:

1. furnace heated part at \( T_0 \): \( \{V/T\}_1 = z_0 \sigma / T_0 \);
2. first exponential part ( \( z_0 \to l \)):

\[
\{V/T\}_2 = \int_{z_0}^{l} \frac{dz}{T(z)} = \frac{\sigma}{T \tau} \ln \left[ 1 + \frac{\bar{T}}{T_0} (e^{\tau(l-z_0)} - 1) \right]
\]

(11)
3. second exponential part ( \( l \rightarrow l' \)):

\[
{V/T}_3 = \int_{l}^{l'} \frac{dz}{T(z)} = \sigma' \cdot \frac{l' - l}{T} \cdot \ln \left[ \frac{T_{ch} - T}{T_{ch}} \cdot \frac{T_{ch}}{T_{ch} - T} \right] \cdot \ln \left( 1 + \frac{T}{T_{0} - T} e^{\tau(l - l_0)} \right)
\]

(12)

4. third exponential part (pipe of length L):

\[
{V/T}_4 = \int_{pipe} \frac{dz}{T(z)} = \frac{V_p}{T} \cdot \ln \left( \frac{T_{ch}}{T_{ch} - T} \cdot \frac{T_{ch} - T_c}{T_c - T} + 1 \right)
\]

(13)

5. cooled volumetric pool at \( T_c \) corresponding to 25°C: \( \{V/T\}_5 = V_s/T_c \)

The effective ”reduced ratio” \([V/T]\), that replaces the ratio \(V/T\) for homogeneous temperature, reads:

\[
\{V/T\} = \sum_{i} \{V/T\}_i
\]

(14)

here:

- \( V_p = V_d - V_H \) - the pipe volume,
- \( \sigma' = \left( \frac{r'}{r} \right)^2 \) - ratio of two inner cross sections of the sample holder,
- \( V_H \) - inner volume of the holder,
- \( V_d \) - the measured ’dead volume’: holder + pipe,
- \( V_s \) - the system volume of the volumetric pool.

For practical purposes we will need also the effective ratio of ”dead volume” \( \{V/T\}_d = V/T - V_s/T_c \):
3.3 Verification of the Model

To construct the effective $V/T$ ratio, as proposed above, only the parameter $T_{ch}$, the temperature at the beginning of pipe channel, has not been measured. For practical calculation it was enough to evaluate this temperature roughly, since this channel is very thin and the final result is not sufficiently affected by some deviation from the exact value $T_{ch}$.

For the initial state with "open valve", the gas in empty (without ad/desorbent) system has a homogeneous temperature distribution with $T = 25^\circ C$ and the pressure $p_{25} = 197$ kPa. If the furnace is set to hold the temperature of $450^\circ C$, the pressure grows up to $p_{450} = 225$ kPa. Since the gas amount remains the same, it is expected, that for effective ratios $\{V/T\}$ it holds:

$$\frac{p_{25}}{p_{450}} = \frac{\{V/T\}_{450}}{\{V/T\}_{25}}$$

(15)

Then we obtained the quotient $p_{25}/p_{450} = 0.8755$. Supposed the $T_{ch} = 150^\circ C$, (that seems to be quite realistic); The model predicts $\{V/T\}_{450} = 9.799 \cdot 10^{-8}$ and for temperature distribution of $T = 25^\circ C$ it provides $\{V/T\}_{25} = 11.116 \cdot 10^{-8}$, the quotient being required is 0.8815. Therefore the agreement between calculated and the experimental data is fairly acceptable.

4 Conclusions

In the current work it has been shown, that the measurement in a typical gas volumetric equipment can be evaluated using the gas equation. The equation is modified by introducing the effective volumetric factor $\{V/T\}$ instead of ratio $V/T$. This factor is calculated with help of the modelling of the temperature profile in the volumetric setup. Using this procedure the effective volumetric factor could be obtained for each heating temperature of the sample holder, as a proper parameter of the volumetric equipment. A pre-calibration with a noble gas before a measurement is not necessary anymore.

References

[1] R. Schulz, S. Boily, J. Huot, patent.publ.no. WO/1998/053299 Int.Appl.No. PCT/CA1998/000505 (26.11.1998)IPC: G01N 15/08
(2006.01), G01N 7/04 (2006.01)

[2] BELSORP-HP manual, BEL Japan,Inc./ 4.15.2008