

## MAGNITUDE OF CHANGE IN VOLUME OF HIGHLY PRESSURIZED GAS CYLINDER DURING VENTING

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**Abstract:** Buoyancy effects due to cylinder expansion are taken into account as an important source of uncertainty in weighing for the preparation of primary or standard gas mixtures by gravimetric methods. Although linear cylinder expansion upon pressurization is known, reliable information on changes in the volumes of gas cylinders is very scarce. We present newly useful information on the magnitudes of changes in the volume depending upon different cylinder materials and volumetric capacities during gas filling and venting. We also found that the literature estimate of about 20 mL for the magnitude of volume expansion for 5-L cylinder capacity at 15 MPa appears significantly overestimated. Our estimate based on the experimental results in this study is within the upper limit of about 14 mL. It is therefore recommended for gas metrology and research communities to use this updated information.

**Keywords:** buoyancy effect, pressurization, expansion, gas mixture.

### 1. INTRODUCTION

Buoyancy effects due to cylinder expansion are taken into account as an important source of uncertainty in weighing for the preparation of primary or standard gas mixtures by gravimetric methods [1]. This buoyancy effect is proportional to the filling pressure [2]. The fractional volume change ( $\Delta V/V$ ) of a gas cylinder is linearly proportional to the difference between the pressure ( $P$ ) in the cylinder and the external pressure ( $P_{\text{ext}}$ ) via:

$$\Delta V/V = K(P - P_{\text{ext}}) \quad (1)$$

where  $K$  is the proportional constant depending on the material, shape and dimensions of the cylinder [3].

Although this relationship is regarded as an established fact, the measurement data are seldom. Section A.5.2.3 of ISO 6142 briefly states that the expansion of the cylinder due to the increase in pressure of 15 MPa (150 bar) will be about 20 cm<sup>3</sup> based on the reference data over 40 years ago [4].

The primary goals of our study are to verify the accuracy of this reported value and to provide detailed information on volume changes that are expected to vary depending upon cylinder characteristics. We therefore tested some commercially available gas cylinders frequently being used

primarily for the preparation of standard gas mixtures. We conducted more than 33 experimental runs to examine the effects of potentially important variables of cylinder material, nominal volumetric capacity, and gas species that affect the magnitude of cylinder volume change. We measured changes in the volumes of 4 different cylinders of different capacities and materials (9.5-L Aluminium, 6.2-L Aluminium, 10.2-L Steel, and 3.4-L Steel) using two different pure gases (N<sub>2</sub> and He) from 12 MPa to 0.1 MPa. All experiments were repeatedly carried out to check reversibility between the expansion and compression of gas cylinder by gas filling about 12 MPa and subsequent venting to atmospheric pressure (0.1 MPa).

### 2. EXPERIMENTAL

A schematic diagram of the experimental setup for a typical experimental run is shown in Figure 1.

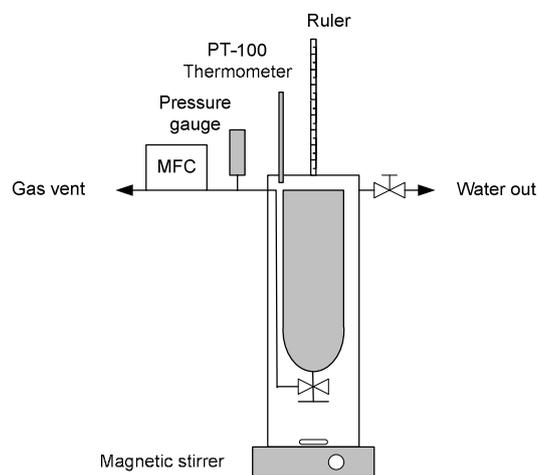


Fig. 1. The experimental set-up for measurement of any change in the cylinder volume during venting.

A test cylinder was pressurized with a filling gas (nitrogen or helium) up to the pressure of 12 MPa. The dimension of the water tank was about 25 L with the radius of 10 cm and the height of 80 cm. Acrylic resin was used for the material of the water tank. A volumetric pipette with the radius of 0.525 cm was vertically positioned in the center of the top of the water tank. The cylinder was connected

through 1/16" stainless tubing to the venting line operated by a mass flow controller (MFC). The water tank was filled up with de-ionized water. The initial water level was adjusted to arbitrary zero position of a ruler attached on the side of the water tank. The cylinder was placed upside down in the water tank. A magnetic stirrer was put into the bottom of the water tank. After the thermal equilibrium was sufficiently reached by agitation with the stirrer, the gas mixture was gradually discharged from the cylinder to the venting line at the volumetric flow rate of 10 L/min via a mass flow controller. During the course of the gas discharge of the cylinder, any change of water height from the original position in the volumetric pipette was monitored every 20 MPa. Synchronously, the temperature of water was monitored with a thermometer to compensate for any thermal effect during gas venting. Any decrease in the gas pressure can lead to the cooling down of the cylinder (i.e., the Joule-Thomson effect) and subsequently water in contact. As a result, water density can be changed, leading to any decrease in the volume water itself.

Any apparent change in the total volume of water and the cylinder caused by cylinder contraction was calculated. Contribution from this effect was subtracted from the apparent volume change.

### 3. RESULTS AND DISCUSSION

#### 3.1. General

It is assumed that the magnitudes of volume changes are identical between cylinder expansion during filling and contraction during venting. This assumption can be at least indirectly validated by checking any reversibility between cylinder expansion during filling and contraction during venting. To this end, we attempted repeated gas filling and subsequent gradual venting under various cylinder settings. Any decrease in the cylinder volume during gas discharge was measured with that in the total volume of water in direct contact with a cylinder in water tank.

#### 3.2. Effect of cylinder pressure and gas species

Any volume decrease in a commercially available aluminium cylinder with 9.5-L capacity during stepwise pressure drop was investigated (Fig. 2) Note that square and circles indicate N<sub>2</sub> and He, respectively and the error bars represent expanded uncertainty ranges from repeated tests ( $k=2$ ). As expected, the contraction of the cylinder was linearly proportional to the pressure in the cylinder. The magnitude of the change in the cylinder volume from the pressure of 12 MPa to atmospheric pressure (0.1 MPa) was about 21 cm<sup>3</sup>. Stepwise gas release tests showed that a linear relationship exist between cylinder pressure and internal volume change.

We also confirmed the reversibility between cylinder expansion and contraction through repetitive gas pressurization and venting operations within the measurement uncertainty ranges represented by the error bars. In addition, it was observed that the magnitude of

volume change of during cylinder contraction is nearly identical regardless of gas species filled within repeatability uncertainty range represented by the error bars.

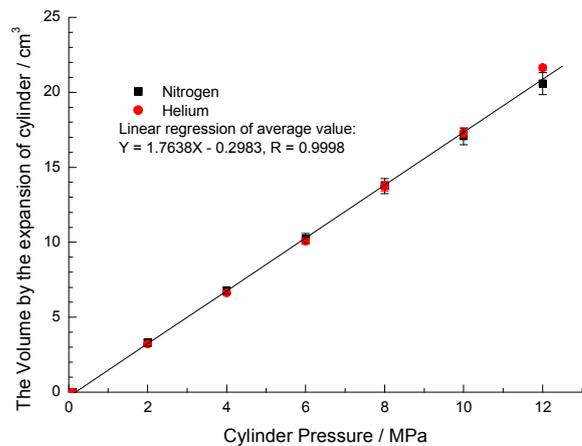


Fig. 2. The volume change of 9.5-L capacity aluminium cylinders during stepwise venting from the initial pressure of 12 MPa.

#### 3.3. Effect of nominal volumetric dimension of cylinder

Any dependence of volume change on cylinder material and volumetric dimension was investigated (Fig. 3). Note that square and circles indicate N<sub>2</sub> and He, respectively and the error bars represent expanded uncertainty ranges from repeated tests ( $k=2$ ). It was observed that the volume contraction of 6.1-L aluminium cylinder from 12 MPa to atmospheric pressure was about 13.5 cm<sup>3</sup>. It was also observed that the volume changes in the aluminium cylinders (Al 9.5 L, Al 6.1 L) were substantially larger than those in the manganese steel cylinders (Steel 10.2 L, Steel 3.4 L). It also appears that the magnitudes of cylinder volume contraction of the same material are roughly proportional to the nominal volumetric capacity. The error bars indicate measurement reproducibility uncertainty ranges for 4 different gas cylinder setting. It appears that the error bars for the manganese steel cylinders were nearly double those for aluminium cylinders. These results suggest that the accuracy of the magnitudes for the volume changes in the aluminium cylinders is better than those in the steel cylinders.

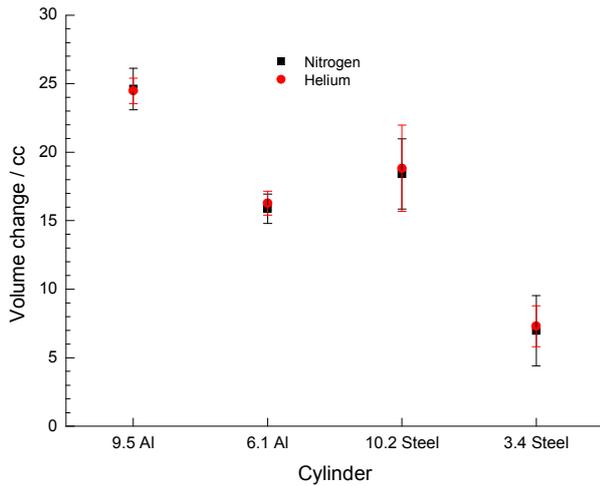


Fig. 3. Dependence of cylinder volume change on volumetric dimension and cylinder material at the pressure of 12 MPa.

#### 4. CONCLUSIONS

It is assumed in this study that the magnitudes of any changes in the internal volume of a gas cylinder during expansion and contraction are virtually identical. It is also assumed that a virtually perfect linearity relationship exists between cylinder volume change and pressure from atmospheric pressure up to 15 MPa regardless of cylinder material and volumetric capacity. Provided that these assumptions are all valid, an extrapolated magnitude of expansion of 5-L cylinder during gas filling from atmospheric pressure to 15 MPa is in the upper limit of about 14 cm<sup>3</sup>. The expected literature value of about 20 cm<sup>3</sup> should be thus regarded as a very rough estimate. The updated information on the magnitudes for cylinder volume changes during pressurization provided in the present study would be useful not only to gas metrology experts especially dealing with gravimetric preparation of standard gas cylinders for international key comparisons, but also to gas physics communities.

#### 5. REFERENCES

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