



Measurements of virial coefficients of Helium, Argon and Nitrogen for the needs of static expansion method

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ABSTRACT

Generally, there are three primary methods in vacuum metrology: mercury manometer, static expansion method, and continuous expansion method. For the pressure below 10 Pa, the idea of the primary standard is that the gas is measured precisely at a pressure as high as possible, and then the gas is expanded to the bigger volumes; this allows to calculate the expanded pressure. An important parameter that needs to be taken care of in primary vacuum calibration methods is the compressibility factor of the working gas. The influence of virial coefficients on the realization of primary standards in vacuum metrology, especially in the realization of the static expansion method is very important. In this paper we will present the measured data for virial coefficients of three gases Helium, Argon and Nitrogen measured at room temperature and a pressure range from 3 kPa to 130 kPa. The dominating term due to real gas properties arises from the second virial coefficient. The influence of higher orders of virial coefficients drops rapidly with lower pressure, particularly for gas pressures values lower than one atmosphere. Hence, in our calculation, the series of real gas was used for the first and second virial coefficients but not for higher-order virial coefficients.

Section: RESEARCH PAPER

Keywords: Real gases; virial equation of state; compressibility factor; virial coefficients

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1. INTRODUCTION

The deviations of real gases from ideal gas behaviour are best seen by determining the compressibility factor [1]:

$$Z = \frac{P V_m}{R T}, \quad (1)$$

where P is the pressure, $V_m(V/n)$ is the molar volume, T is the temperature, and R is the universal gas constant. At low pressures and high temperatures, the ideal gas law can adequately predict the behaviour of natural gas. However, at high pressures and low temperatures, the gas deviates from the ideal gas behaviour and is described as real gas. This deviation reflects the character and strength of the intermolecular forces between the particles making up the gas. Several equations of state have been suggested to account for the deviations from ideality. A very handy expression that allows for deviations from ideal behaviour is the virial equation of state [2]. This is a simple power series expansion in either the inverse molar volume, $1/V_m$:

$$Z = \frac{p V_m}{R T} = A + \frac{B}{V_m} + \frac{C}{V_m^2} + \dots, \quad (2)$$

or the pressure, p :

$$Z = \frac{p V_m}{R T} = A' + B'p + C'p^2 + \dots, \quad (3)$$

with A, A' - first virial coefficient, B, B' - second virial coefficient, C, C' - third virial coefficient. All virial coefficients are temperature-dependent. According to statistical mechanics, the first virial coefficient is related to one-body interactions, the second virial coefficient is related to two-body interactions and the higher virial coefficients are related to multi-body interactions [1], [3]. The main goal of this experiment is to determine values for the second virial coefficient B of gases Helium, Argon and Nitrogen at room temperature. The second virial coefficient has a theoretical relationship with the intermolecular forces between a pair of molecules which can provide quantitative information on these forces.

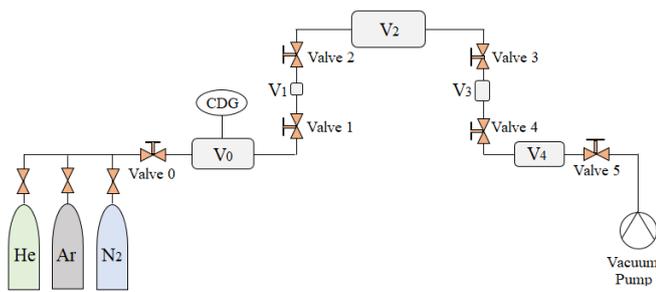


Figure 1. Schematic illustration of the experimental setup. Valves 1, 2, 3 and 4 are installed between the chambers V_0 , V_1 , V_2 , V_3 and V_4 . The capacitance diaphragm gauge (CDG) is attached to the chamber V_0 . A black rubber hosing connects the gas regulator to valve 0 and a flexible metal hose is used from valve 5 to the turbomolecular vacuum pump.

The results will serve the scientific community in the field of metrology for the most accurate measurement standards in vacuum metrology, in atomic physics will show the level of interaction of atoms and molecules of certain gases, and in the chemical aspect we will gain knowledge about behaviour of gases at different pressures; in this way, it will be possible to obtain information about the limit of transition from ‘ideal gas’ to ‘real gas’ and vice versa.

2. EXPERIMENTAL SETUP

A schematic illustration of the experimental setup is shown in Figure 1. Our system comprises five chambers (V_0 , V_1 , V_2 , V_3 and V_4) of significantly different sizes, the volumes of which have been determined by using the gas expansion method. The vacuum isolation valves are installed between the chambers, and a turbomolecular pump (HiCube Eco) is connected to valve 5. A capacitance diaphragm gauge (CDG025D) is attached to the chamber V_0 to measure the precise pressure before and after expansion. The whole experiment was performed under well-controlled ambient temperature in the air-conditioned laboratory. In order to reduce the temperature drifts and transient local heating during the working day, we kept all electrical equipment (pump and lights) switched on at all times (24 h/day). The average temperature was 296 K and the pressure range was from 3 kPa to 130 kPa [4].

3. VOLUME DETERMINATION

To determine the volume of vacuum chambers, we must know the value of one of the volumes. We measured the geometrical dimensions of the known volume V_0 by using a calibrated caliper. A cylinder with radius r and height h has a volume given by $V_0 = \pi r^2 h$. Using the dimensions of the volume V_0 we have calculated mean value of the volume $V_0 = 0.71$ l with associate uncertainty 0.14 % for coverage factor $k =$

Table 1. Mean value, standard deviation and uncertainty of volumes.

	\bar{x}	δ	u
V_0 (l)	0.7100	$9.61 \cdot 10^{-4}$	$1.36 \cdot 10^{-3}$
V_1 (l)	0.0668	$5.82 \cdot 10^{-5}$	$8.71 \cdot 10^{-4}$
V_2 (l)	0.7879	$2.04 \cdot 10^{-3}$	$2.59 \cdot 10^{-3}$
V_3 (l)	0.1652	$2.82 \cdot 10^{-3}$	$1.71 \cdot 10^{-2}$
V_4 (l)	0.5416	$5.48 \cdot 10^{-3}$	$1.01 \cdot 10^{-2}$

1. All the uncertainties throughout this paper are given for coverage factor $k = 1$ [1], [4].

Therefore, to determine volumes V_1 , V_2 , V_3 and V_4 we used the static expansion method. In this method, the pressures before and after the expansion are used for determining the expansion ratio. The gas is first enclosed in the smaller volume, then it is allowed to enter the larger volumes to expand under nearly perfect isothermal conditions [5]. This procedure is applicable only if the pressure after expansion can be measured with about the same accuracy as the pressure before expansion. Argon is used as a gas for this type of calibration, although helium and nitrogen could also be used. The purity of the argon gas was 5.0 N (99.999 %). The mean values, standard deviation and uncertainty of volumes of the five vacuum chambers are given in Table 1. The measurement uncertainty depends on the ratio of volumes (pressures before and after expansions) [6].

4. COMPRESSIBILITY FACTOR

In this section, an analytical approach for calculating the compressibility factor of gases is presented. In this experiment, the gas was expanded four times in different volumes. The experimental procedure can be described as follows. In the beginning, all valves are opened and the entire system is pumped down to less than 10^{-5} Pa. Valves 2, 3, 4, 5 are closed, valves 0, 1 are opened and gas comes out very quickly into $V_0 + V_1$. With the left hand, a knob has adjusted the regulator to fill the system at a pressure of a little over 130 kPa. The pressure is monitored for a few minutes until is stable, then is recorded as p_1 . The ambient temperature T is also recorded. Then valve 2 is opened and the gas expanded into $V_0 + V_1 + V_2$. Again, after equilibrium, the pressure is recorded as p_2 . Then valve 3 is opened and gas is expanded into $V_0 + V_1 + V_2 + V_3$. When equilibrium is reached the pressure is recorded as p_3 . For the final measurement, valve 4 is left open and the gas expanded into all volumes $V_0 + V_1 + V_2 + V_3 + V_4$. After the gas is expanded in the entire system, pressure dropped below 3 kPa and is recorded as p_4 . This procedure is repeated nine times, and the equilibrated pressures are recorded at each stage [7], [8]. For pressure measurements, we have used CDG025D with an uncertainty of 0.2 % [9].

Once each gas transfer pressure is measured, the volumes and temperature are also known, we need only the number of moles of gas to find directly its compressibility factor Z . From the general gas equation, we obtain the expression for the amount of substance:

$$n = \frac{p V T_0}{T P_0 V_0} \quad (4)$$

where T_0 is the standard temperature, P_0 is the standard pressure and V_0 is the molar volume at STP [1].

After we obtained the complete data set P , V , T and n , the compressibility factor is calculated by using equation (1). Plots of compressibility factor (Z) as a function of inverse molar volume ($1/V_m$) for (a) Helium, (b) Argon and (c) Nitrogen are presented in Figure 2. For these real gases in the graphs, we notice that the shapes of the curves look a little different for each gas, and most of the curves only approximately resemble the ideal gas line at $Z = 1$ over a limited pressure range [10]-[12].

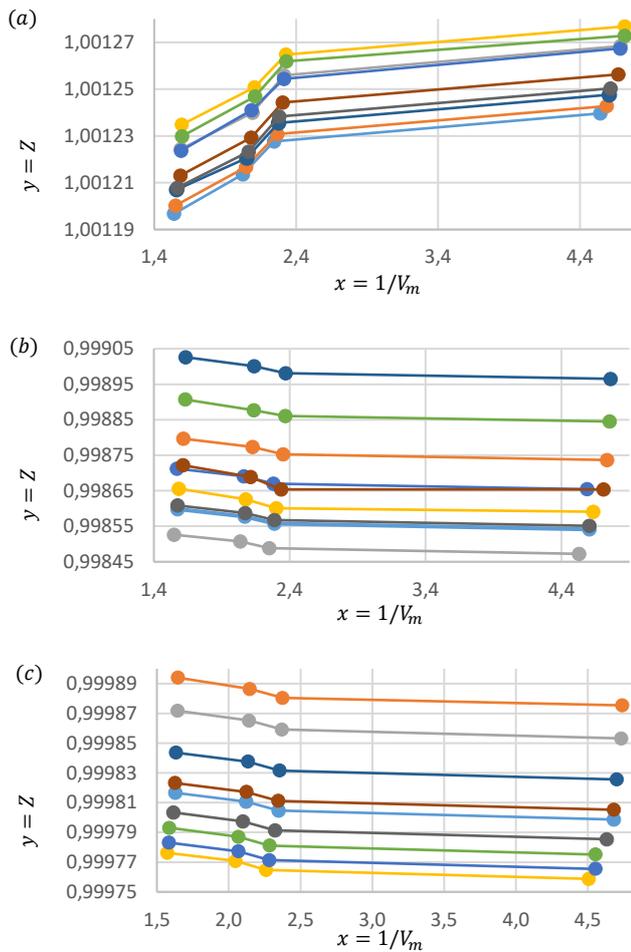


Figure 2. The compressibility factor, Z , as a function of inverse molar volume ($1/V_m$) for (a) Helium, (b) Argon and (c) Nitrogen.

5. RESULTS

5.1. Calculation of Virial Coefficients

At low pressures, e.g. below two atmospheres, the third and all higher virial terms usually may be neglected; hence, the equation of state (2) becomes:

$$Z = \frac{pV}{nRT} = A + \frac{B}{V_m} + \dots \quad (5)$$

Using spreadsheet software such as Excel, we plotted Z as a function of $1/V_m$ for each trial. For each gas, some curvature is observed, and we determined values for both the first (A) and second (B) virial coefficients. Using the LINEST function in Excel, we determined the values and standard deviations of the slope and y-intercept in a linear fit. By properly combining values of B and their uncertainties from multiple trials, an average value of this coefficient and its standard deviation for each gas was calculated [1], [3].

The mean value, standard deviation and uncertainty of the first and second virial coefficients for these three gasses are summarized in Table 2. Figure 3 shows values of the second virial coefficient for (a) Helium, (b) Argon and (c) Nitrogen at room temperature.

Table 2. Mean value, standard deviation and uncertainty of A and B coefficients for Helium, Argon and Nitrogen.

		\bar{x}	δ	u
<i>He</i>	A	1.00120	$1.26 \cdot 10^{-5}$	$4.22 \cdot 10^{-6}$
	B (m^3/mol)	$1.16 \cdot 10^{-5}$	$2.33 \cdot 10^{-7}$	$7.78 \cdot 10^{-8}$
<i>Ar</i>	A	0.99871	$1.63 \cdot 10^{-4}$	$5.42 \cdot 10^{-5}$
	B (m^3/mol)	$-1.61 \cdot 10^{-5}$	$3.75 \cdot 10^{-7}$	$1.24 \cdot 10^{-7}$
<i>N₂</i>	A	0.9998	$3.75 \cdot 10^{-5}$	$1.25 \cdot 10^{-5}$
	B (m^3/mol)	$-5.1 \cdot 10^{-6}$	$7.25 \cdot 10^{-8}$	$2.41 \cdot 10^{-8}$

6. DISCUSSION

In Table 3, the experimental values obtained in this work for second virial coefficients are compared with values from the literature [1], [13]-[17]. It can be seen the experimental results show good agreement with the data in the literature.

According to the above results, it is possible to make the following considerations:

- The compressibility factor of helium is greater than 1, which shows that repulsive forces dominate between molecules and atoms. Whereas for argon and nitrogen the value of Z is lower than 1, in this case, the attractive forces are stronger (Figure 2).
- At room temperature, the second virial coefficient is positive for helium and negative for argon and nitrogen (Figure 3).

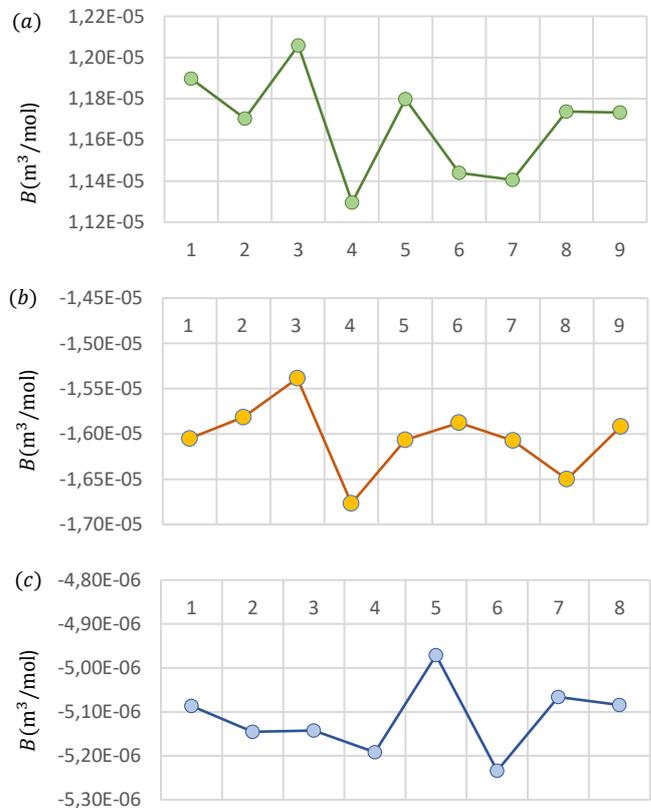


Figure 3. Values of B coefficient for (a) Helium, (b) Argon and (c) Nitrogen at 296 K.

Table 3. Comparison between experimental values of second virial coefficients and literature values.

	T (K)	B in 10 ⁻⁶ (m ³ /mol)		
		He	Ar	N ₂
Literature	293	11.2 ^[14]	-16.9 ^[14]	-6.1 ^[14]
	296	11.7 ^[13]	-16.0 ^[13]	-5.0 ^[13]
	298	11.8 ^[15]	-15.8 ^[16]	-4.5 ^[16]
	300	11.9 ^[17]	-15.7 ^[1]	-4.7 ^[1]
This work	296	11.6	-16.1	-5.1

7. CONCLUSIONS

Based on the obtained experimental data, the pressure that is generated in the primary pressure standard for these initial pressure values must be corrected at most up to 0.005% since the deviation of the real gas from the ideal behaviour is very small. The gas with the smallest deviation from the ideal behaviour was nitrogen with a correction of about 0.001%: based on these results, we are going to use nitrogen in future calibration procedures.

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