CORRIGENDUM

Corrigendum: compressibility of gas mixtures pertaining to nuclear fuel rods (2020 J. Phys. Commun. 4 095008)

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A series of errors were discovered once the paper described above was published. The corrections to these errors are listed below.

1. Line 4 in the abstract describes one of the gas mixtures as 11.3%He:12.9%Xe:75.8%Kr. The gas mixture should be 11.3%He:12.9%Kr:75.8%Xe

2. Line 2 in the first paragraph of section 5.2 discusses a He:Kr gas. It should be a Xe:He gas.

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Compressibility of gas mixtures pertaining to nuclear fuel rods

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Abstract
Gas pressure inside an irradiated nuclear fuel rod impacts its performance and safety. To accurately assess the pressure inside a rod, the temperature, composition, quantity, volume, and compressibility of a gas must be determined. The compressibility of a pure gas, Ar, and gas mixtures; 98%Ar:2%H2, 50%Xe:50%He, and 11.3%He:12.9%Xe:75.8%Kr, were experimentally derived in the pressure range of 65 to 10,400 kPa at 293.7 ± 1.5 K isotherm. The Analytical Research Laboratory at Idaho National Laboratory has been performing gas compressibility experiments to improve plenum-pressure determination of fuel rods. For each gas mixture, the compressibility was calculated for a series of pressure measurements. A second-order polynomial function was fit to the data set, allowing for the determination of the first-, second-, and third-order virial coefficients and their uncertainties. This method for determining virial coefficients and their application for determining plenum-gas pressures refines previous methods.

1. Introduction
The composition and pressure of gas contained inside irradiated nuclear fuel-rod assemblies has an important effect on the design and engineering of the rod and its containment [1–3]. Characteristics of the gas inside a fuel-rod plenum will vary based on the composition, original gas back-fill parameters, and degree to which the rod was irradiated (burnup). One method of studying these effects was to build a test rod, irradiate the rod in a reactor, and quantitatively collect the gas contained in the rod. The composition and quantity of the gas collected can then be used to model properties of a fission gas in the pressurized fuel rod. The properties of the plenum gas may be correlated to the conditions under which it was irradiated. Previous testing has focused on calculating the quantity of gas inside the plenum. These calculations were derived from measurements taken when the gas was in a condition where the ideal equation of State (EOS), also known as the ideal gas law, adequately described the behavior of the gas. The ideal gas law, as described by the kinetic theory of gases, given in equation (1):

\[ pV = nRT \]  \hspace{1cm} (1)

where \( p \) is pressure (kPa), \( V \) is volume (cm\(^3\)), \( n \) is the number of moles of gas (mol), \( R \) is the ideal gas constant (J mol\(^{-1}\) K\(^{-1}\)), and \( T \) is absolute temperature (K) [4–7]. Improved modeling of fuel-rod conditions, including plenum pressure, has necessitated more-accurate information about the behavior of the gas contained within the rod. Equation (1) does not adequately describe gas systems, which exhibit significant interactions, both repulsive and attractive forces, at the elevated pressures seen inside nuclear fuel rods [8, 9]. The compressibility of a gas describes the degree to which a gaseous atom or molecule can be packed inside a fixed volume and is inversely related to its molar volume [10]. When accounting for compressibility in the ideal EOS, the equation takes the form of equation (2):
where $Z$ was the compressibility factor [11]. For ideal conditions, $Z = 1$ and equation (2) reduces to the ideal gas law shown in equation (1) [12].

The EOS for a gas mixture sealed inside a fixed volume is dependent upon temperature, pressure, volume, quantity, and composition of the mixture. To determine $Z$ for a gas system, the volume of the sealed system was enlarged until ideal pressure conditions were obtained while maintaining temperature and moles of gas constant. If both the initial ($V_{\text{initial}}$) and final ($V_{\text{ideal}}$) volumes were known, then the compressibility of the initial system can be calculated using equation (3):

$$Z = \frac{V_{\text{initial}} \cdot P_{\text{initial}}}{V_{\text{ideal}} \cdot P_{\text{ideal}}}$$

(3)

As conditions deviate from an ideal state towards higher pressures (typically >101 kPa) and lower temperatures (typically <273 K) the EOS becomes increasingly more difficult to predict and has typically modeled with a virial equation derived from empirical data. In terms of pressure, the virial equation takes the form of equation (4):

$$Z = A + Bp + Cp^2 + \ldots$$

where $A$, $B$, and $C$ were referred to as the first-, second-, and third-order virial coefficients, respectively, and are calculated by regression analysis of the plots of pressure versus $Z$ [13, 14]. Equation (4) was valid only for the temperature isotherm and gas-mixture conditions under which the data were collected. Variability in the virial equation of a gas can be linked to many sources, and has been studied extensively for pure gases and simple gas mixtures [15–19]. However, the availability of data on the virial coefficients of many gas mixtures was absent from the literature due to the number of variables and complexity of their EOS.

In this paper the compressibility of pure Ar and several gas mixtures were calculated. Pure Ar was used as an initial test case based on its cost, frequent use, and the availability of its previously published data for comparison [14, 20]. The mixtures were chosen based on several factors, including their predicted compressibility, applicability to current research projects, and potential interactions with system components used in plenum-gas collection instruments. The compressibility factors were reported throughout the range of pressures and were used to determine the first-, second-, and third-order virial coefficients. The total expanded uncertainty for the compressibility and virial coefficients was determined using a GUM software package and was reported herein.

2. Material and methods

Gas standards were obtained from Specgas, Inc., with certified concentrations for each gas and used as received. A ~5 cm$^3$ stainless-steel vessel with a vacuum coupling radiation (VCR) fitting was manufactured at Idaho National Laboratory and attached to a high-pressure quarter turn diaphragm valve, Swagelok model 6LW- DPHVR4-P. Before use as a volume standard, the vessel was calibrated at Sandia National Laboratories’ Primary Standards Laboratory, providing a certificate of analysis traceable to National Institute of Standards and Technology (NIST). Two MKS Instruments absolute Baratron® capacitance manometers with 0.12% relative accuracy were utilized for pressure measurements in the expansion of pure and mixed gases. A power supply and pressure readout, MKS Instruments model PR4000B-F2V2, connected to both a 0–138 kPa range Baratron® capacitance manometer, MKS Instruments model 627F13TBCB, and a 0–2670 kPa range Baratron® capacitance manometer, MKS Instruments model 627F24TBCB2B. The 0–138 kPa range Baratron® capacitance manometer was used for pressure measurements less than 70 kPa, and the 0–2670 kPa range Baratron® capacitance manometer was used for pressure measurements between 138 and 1380 kPa. A 0–13,800 kPa range pressure transducer, Honeywell Model STJE, having a 0.05% full-range absolute error with a power supply and readout, Honeywell model SC500, was used for all pressure measurements greater than 1380 kPa. Calibration of the pressure sensors and their readouts were maintained as a set during the experiments by comparison with NIST-traceable standards. A custom Resistance Temperature Detector (RTD) probe produced by Idaho Laboratories Corporation and coupled to a Digi-Sense Temp-16 RTD thermometer readout was used for all temperature measurements. The system was calibrated by comparison to NIST-traceable sources over the 273–373 K range. Burst discs were installed on the manifold for personnel safety and equipment protection. High-vacuum conditions (<1.0E-8 kPa) were obtained using a Pfeiffer brand turbo and scroll pump. A recirculating water chiller with an open bath containing the volume standard and a ~500 cm$^3$ expansion volume was used to thermally regulate the system while manifold temperature was maintained at 293.7 ± 1.5 K, as measured by the RTD, during all expansions.

All uncertainty analyses were performed using GUM Workbench, Version 2.4.1.406, and reported as expanded uncertainties ($k = 2$). This method allows for an accurate assessment of the uncertainty in the
experiment by accounting for all sources and provides a value with an uncertainty at a 95% confidence level. Temperature, pressure, and volume uncertainties were used as specified on the certificate of calibration. Uncertainties determined from volume calibrations were propagated into the compressibility calculation and virial coefficients. Uncertainty for the virial coefficients were calculated using a standard method [21].

3. Experimental

3.1. Volume calibration

Figure 1 details the gas manifold used during the experiments. The internal volume of the manifold was determined using a gas-expansion method and the certified volume standard. Multiple sections of the manifold were determined to accommodate the range of starting pressures, from 70 to 10,350 kPa, used in these experiments. An uncertainty budget for each volume determination was calculated using the GUM workbench.

The gas-expansion method was a multistep process in which the system to be determined was first evacuated and the certified volume standard pressurized with gas and then expanded into the evacuated portion of the manifold volume to be determined. Expansions were performed using ultra high purity (UHP) Ar gas at final pressures less than 107 kPa, at which the compressibility of the gas was negligible. The combined gas law, equation (5), was used to determine the expanded volume of the manifold, inclusive of the volume standard:

\[
\frac{P_I V_I}{T_I} = \frac{P_F V_F}{T_F}
\]

where \(I\) indicates the initial conditions and \(F\) indicates the final conditions. Rearrangement of equation (5) shows this calculation explicitly, as shown in equation (6):

\[
V_F = \frac{P_I \times T_F}{P_F \times V_F \times T_I}
\]

Using this method, the volume-measurement uncertainty was minimized, with the major contribution (over 90%) to the expanded uncertainty being dominated by the volume of the certified volume standard.

3.2. Compressibility

Compressibility was determined after an accurate assessment of the volume and uncertainty calculations were complete. The following method was used for all compressibility determinations. The manifold was evacuated to less than 1E-8 kPa prior to any expansion or pressurizing of the gas. Once expanded or pressurized, the system was allowed to thermally equilibrate before isolation and/or measurements were performed. The certified volume standard was pressurized to within \(\pm5\)% of a target pressure. Temperature and pressure of the manifold were measured after isolation of the volume standard from the manifold. The manifold, except the certified volume standard, was then evacuated to less than 1E-8 kPa. The gas contained in the certified volume standard was expanded into a predetermined volume sufficient to reduce the final pressure of the system to less than 107 kPa. When gases at pressure greater than 3450 kPa were expanded, a precipitous drop in temperature was observed, necessitating an extended equilibration time. The final expanded pressure and temperature were recorded. Compressibility of the gas was then calculated using equation (7):
Table 1. Virial coefficients calculated from experimental data, with uncertainty listed at k=2.

| Gas Composition       | A Intercept  | B (Pa⁻¹)     | C(Pa⁻²)     |
|-----------------------|--------------|--------------|-------------|
| UHP argon             | 1.000 ± 0.002| -4.10E-9 ± 3.1E-9| 1.1E-16 ± 3.0E-16|
| 98.0%Ar:2.0%H₂        | 1.002 ± 0.006| -9.63E-9 ± 1.2E-8| 1.1E-15 ± 3.4E-16|
| 49.9%Xe:50.1%He       | 0.996 ± 0.005| -6.1E-9 ± 3.2E-9| 3.6E-16 ± 3.3E-16|
| 11.3%He:12.9%Kr:75.8%Xe| 1.002 ± 0.006| -3.4E-8 ± 1.2E-8| -1.9E-15 ± 3.3E-15|

\[ Z = \frac{P_i * V_{STD}}{T_i * n_{ideal} * R} \]  

(7)

where \( P_i \) and \( T_i \) were initial pressure and temperature, respectively, \( V_{STD} \) was the volume of the certified volume standard, \( R \) was the gas constant, and \( n_{ideal} \) was the number of moles calculated after expansion to pressures less than 107 kPa. The compressibility factor \( (Z) \) and associated uncertainty for each expansion were determined and plotted against the pre-expanded pressure. Fitting a second-order polynomial equation to the data set allows for determination of pressure-dependent virial coefficients, which define the behavior of the gas or gas mixture within the range of empirical data. Extrapolation of this type of equation was inadvisable as many gases were known to exhibit inflection points in the virial equation. Thus, virial coefficients for a gas or gas mixture were not applicable outside the isotherm, range of pressures, and specific gas composition experimentally examined.

4. Results

Three theoretical EOS models: van der Waals (VDW), Redlich-Kwong (RK) [22], and Peng-Robinson (PR) [23], were used in comparison with the experimentally determined compressibility for Ar. Reengagement of these equation allowed for the calculation of a theoretical \( Z \) at each of the desired pressures [24]. At pressures below 725 kPa, the VDW agreed well with the data. Starting at 725 kPa, the VDW began to diverge from the experimental data. Theoretical results from both the RK and PR models agree to within 1% of the experimental data. The experimentally determined virial coefficients, as shown in table 1, agree with those in previously reported data [25].

Once the virial calculations were completed for Ar, and confirmation of their agreement with the EOS models (PR and RK) was confirmed, the virial coefficients for gas mixtures Ar:H₂, Xe:He, and He:Kr:Xe were performed, using the same method. These were also reported in table 1.

5. Discussion

The purpose of this paper was to develop a method by which the pressure of a non-ideal gas in a sealed system (fuel rod plenum) can be determined. In order to validate the method, the virial coefficients for UHP Ar gas were calculated and compared to theoretical models derived by PR and RK. All gas mixtures were chosen based on their expected non-ideal behavior at elevated pressure. Ar:H₂ was of interest due to other test cases, beyond the scope of this paper, while the noble gas mixtures were similar to fission-gas compositions.

5.1. Argon

Initial evaluation of the method used UHP Ar as the test gas. Theoretical compressibility factors for Ar were calculated using the RK and PR in a straightforward method, as described above. For all pressures tested, the calculated compressibility factors have overlapping uncertainty; however, a general trend away from ideal, \( Z = 1 \), was observed over the measurement range. As shown in figure 2, this agrees well with the RK and PR equations. Agreement between experimental results and the theoretical models provided validity to the method used. Modeling of the Ar gas using the VDW equation resulted in deviation of the model from experimental data at pressures above 3450 kPa, which was not unexpected, as the attractive and repulsive interactions present in real gases were less accurately modeled by the VDW than the RK and PR [22, 23]. Comparison of the experimental data with EOS models shows a greater efficacy for the PR model. The agreement between experimental data and PR was not overly surprising as the PR was a refinement of the RK model with respect to the repulsive/attractive factors used in the equation. Given the agreement between the PR and the calculated virial equation, evaluation of the system with a more refined EOS was unnecessary.

5.2. Gas mixtures

The compressibility for the two-component gas mixtures shows similar behavior to one another and to UHP Ar as pressure was increased. The similarity in the compressibility of the He:Kr gas with the UHP Ar and Ar:H₂ gas...
provides an interesting comparison because it contains drastically different composition, but exhibits similar behavior, as shown in figure 3.

The three-component gas mixture begins to show deviation from ideal behavior near 345 kPa. With an increase in pressure, the deviation from ideal behavior becomes more pronounced in the three-component than the two-component gas mixture. The deviation of the three-component gas compressibility from ideal, \( Z = 1 \), near 3450 kPa was approximately \(-15\%\), as shown in figure 3.

The magnitude of change in compressibility when comparing the two- and three-component gas mixtures provides an example of the impact an additional gas component can have on system behavior. Kr and Xe are large polarizable gases and were expected to exhibit less-ideal behavior. He, however, is a small gas more accurately modeled by the ideal gas law, compared to Kr and Xe [16, 26].

A likely explanation for the lower compressibility factor of the three-component gas mixture was the lower He content, which was amplified by the high concentration of Kr and Xe. The three-component mixture provides a more accurate surrogate for irradiated fuel than the two-component mixtures, as both Kr and Xe production are significant during U-235 fission. Fuel rods are often backfilled with He due to its inert chemical behavior and favorable thermal conductivity.

5.3. Virial equations

Compressibility of a gas in relation to its pressure, as shown in figures 2 and 3, can be described by a polynomial equation to determine the virial coefficients shown in equation (4). The equation is generally limited to the first- and second-order virial coefficients. The third-order virial coefficient was used when a more accurate model of the compressibility was needed. For more complex systems (i.e., those with more constituents or diverging behavior), the number of virial coefficients required to accurately model the behavior of the gas was needed. In this study, third-order virial coefficients were reported for all test gases to ease comparison.

6. Conclusions

The compressibility and virial equation for Ar agrees well with theoretical models, validating the method used to determine the compressibility of the other gas mixtures. Differences in gas composition were shown to have a significant effect on the characteristics of the gas as pressure increases. For the two-component mixtures, the compressibility trends away from \( Z = 1 \) as the pressure increases. In comparison to the three-component mixture, this trend was not as pronounced, but was sufficient to result in significant impact on engineering characteristics. Previous testing on irradiated plenum-gas characterization was incomplete. The inclusion of gas compressibility into models describing sealed gas systems, such as fuel rods, can drastically improve their accuracy and the engineering tasks for which they were used.
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Data availability

The raw/processed data required to reproduce these findings cannot be shared at this time as the data also forms part of an on-going study.

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Figure 3. Experimental compressibility factors for two-component (Top) and three-component (Bottom) gas mixtures with their corresponding virial equation fit line.
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