Determination of Ar molar mass for the Boltzmann constant

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Acoustic determination of $k$ and molar mass of argon

$$k = \frac{c_0^2 M}{T \gamma_0 N_A}$$

Measured $k$ is proportional to $M$, molar mass of thermometric gas. Thus, $u(M)$ directly adds into $u(k)$.

The $u(k)$’s in argon-based measurements, except for NIST-88, are based on uncertainty assigned at KRISS, $u_r(M) = 0.7 \times 10^{-6}$

Yang, Pitre, Moldover, Zhang, Feng, Kim, Metrologia, 2015, Vol. 52, S394-409

Note: $u_r(k_{\text{CODATA-2014}}) = 0.57 \times 10^{-6}$
Motivation of the work

- Provide better $M$ measurement (lower uncertainty) for acoustic determination of $k$, if needed.

- Complete a procedure of the molar mass measurement, to make sure the method and uncertainty assessment are sound from perspective of thermometry.

Reference “R3”

\[
\frac{^{40}\text{Ar}}{^{36}\text{Ar}} = 330.30 \pm 0.34
\]

Reference “R2”

\[
\frac{^{40}\text{Ar}}{^{36}\text{Ar}} = 39.596 \pm 0.037
\]


Gravimetric method

Molar mass of argon determination for Boltzmann project in 2014
Mass spectrometer at KRISS

- Finnigan MAT 271 mass spectrometer
- Works for all mass/charge ratio
- Good linearity (works for dynamic range of 5.5 decade)
- Moderate repeatability

“Partial pressure” machine

Pressure of certain gas in the sample

Ion current (Number of ion per second) (Output voltage)

- Sensitivity slowly changes over time.
- Sensitivity of isotopes are not the same.

➤ We need reference gas.
“Calibration of mass spectrometer”

Reference of known

\[ R_{40/36} \text{ ratio } = \frac{\text{amount of } ^{40}\text{Ar}}{\text{amount of } ^{36}\text{Ar}} \]

Measure Ion current ratio \( I_{40} / I_{36} \)

\[ K_{36} = \frac{\text{known } R_{40/36} \text{ ratio}}{\text{Measured ion current ratio } I_{40} / I_{36}} \]

\( K_{36} \) is very closed to 1, but not identical to 1. 
\( K_{36} = 0.9932 \), for example, and changes with time.

For samples,

\[ R_{40/36} = K_{36} \times I_{40} / I_{36} \]

- Ideally, with a similar procedure, we can obtain \( K_{38} \).
- But for all practical reasons, we use \( K_{38} = (1 + K_{36}) / 2 \).

Assumed linearity of sensitivity change

narrow range
same kind of molecule (argon)
Sensitivity of isotopic ratio and target uncertainty of molar mass

\[ M_{Ar} = \frac{M_{36} + R_{38/36} M_{38} + R_{40/36} M_{40}}{1 + R_{38/36} + R_{40/36}} \]

Near a “natural” isotopic composition,

- 0.1 % of \( R_{40/36} \) of \( M_{Ar} \)
- 0.1 % of \( R_{40/36} \)
- \(-0.032 \times 10^{-6}\) of \( M_{Ar} \)

We want to determine \( R_{40/36} \) of sample within 0.05 %

\[ u(R_{40/36})_{sample} = 0.15 \] (0.156 % in 2014 measurement)

For this, we need reference of known \( R_{40/36} \) better than 0.05 %

\[ (R_{40/36})_{reference} = 300 \pm 0.1 \]
Gravimetric method

Known $R_{40/36}$ ratio by gravimetric method

ISO 6142-1 Gas Analysis – Preparation of calibration gas mixtures – Part 1: Gravimetric method for class 1 mixtures
Gravimetric method

Known $R_{40/36}$ ratio by gravimetric method

Two references were prepared:
one with $R_{40/36}$ slightly above atmospheric ratio (R4),
one slightly below (R5)

ISO 6142-1 Gas Analysis – Preparation of calibration gas mixtures – Part 1: Gravimetric method for class 1 mixtures
Weighing cylinders: comparison against “tare” cylinder

• Always comparison against a tare cylinder
• Tare always moves together with cylinders to be measured. (buoyancy compensation)
• Tare → cylinder 1 (→ cylinder 2) → Tare → cylinder 1 (→ cylinder 2) → Tare → ... cycle repeated
• Automatic weighing system to minimize interference

Balances (mass comparator) used:

Mettler Toledo AX1005
1.1 kg capacity, 0.01 mg resolution

Mettler Toledo XP10003S:
10.1 kg capacity, 1 mg resolution
## Source gas

Enriched argon sources purchased from ICON services Inc. (NJ, USA)

<table>
<thead>
<tr>
<th>Element</th>
<th>Container</th>
<th>Pressure</th>
<th>Nominal chemical purity</th>
<th>Nominal isotopic purity</th>
<th>Usage</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{40}$Ar</td>
<td>1.4 L</td>
<td>7.1 MPa</td>
<td>99.9 %</td>
<td>99.96 %</td>
<td>For purging only</td>
</tr>
<tr>
<td>$^{40}$Ar</td>
<td>3.03 L</td>
<td>6.6 MPa</td>
<td>99.9 %</td>
<td>99.96 %</td>
<td>Source gas</td>
</tr>
<tr>
<td>$^{36}$Ar</td>
<td>0.5 L</td>
<td>1 MPa</td>
<td>99.9 %</td>
<td>99.95 %</td>
<td>Purging and source gas</td>
</tr>
</tbody>
</table>
Filling $^{36}$Ar and weighing

- $^{36}$Ar source
- tare
- 0.075 L Cylinder 1
- 0.075 L Cylinder 2
Filling $^{36}\text{Ar}$ and weighing

Mass of $^{36}\text{Ar}$ measured by differential measurements of 0.075 L cylinders

$^{36}\text{Ar}$ in cylinder 1: 0.147 07 g
$^{36}\text{Ar}$ in cylinder 2: 0.147 75 g
Filling $^{40}\text{Ar}$ and weighing
Filling $^{40}$Ar and weighing

- $^{36}$Ar transferred from 0.075 L cylinder to 1 L cylinder
- Mass of $^{40}$Ar measured by differential measurements of 1 L cylinder

$^{40}$Ar in cylinder R4: 50.852 68 g
$^{40}$Ar in cylinder R5: 49.684 83 g
Mechanical mixing

Rolling for a few hours for homogeneous mixture
Effect of chemical impurity and isotopic impurity

For 10 μmol/mol existence in the source, the shift in $R_{40/36}$ is ...

\[
y_k = \frac{\sum_{j=1}^{r} x_{k,j} \times m_j}{\sum_{j=1}^{q} \left( \frac{x_{i,j} \times M_j}{\sum_{i=1}^{r} x_{i,j} \times M_j} \right)}
\]

<table>
<thead>
<tr>
<th>Element</th>
<th>In $^{40}$Ar cylinder</th>
<th>In $^{36}$Ar cylinder</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$</td>
<td>0.0002</td>
<td>0.0002</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>0.0014</td>
<td>0.0014</td>
</tr>
<tr>
<td>CO</td>
<td>0.0021</td>
<td>0.0023</td>
</tr>
<tr>
<td>N$_2$</td>
<td>0.0021</td>
<td>0.0023</td>
</tr>
<tr>
<td>O$_2$</td>
<td>0.0024</td>
<td>0.0026</td>
</tr>
<tr>
<td>$^{36}$Ar</td>
<td>0.8729</td>
<td>-</td>
</tr>
<tr>
<td>$^{38}$Ar</td>
<td>0.0028</td>
<td>0.0030</td>
</tr>
<tr>
<td>$^{40}$Ar</td>
<td>-</td>
<td>0.0032</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>0.0032</td>
<td>0.0035</td>
</tr>
<tr>
<td>Kr</td>
<td>0.0061</td>
<td>0.0067</td>
</tr>
<tr>
<td>Xe</td>
<td>0.0095</td>
<td>0.0105</td>
</tr>
</tbody>
</table>

The most significant “impurity” is $^{36}$Ar in $^{40}$Ar cylinder.

Remember: target uncertainty of $R_{40/36}$ is 0.1
## Preliminary analysis

<table>
<thead>
<tr>
<th>Element</th>
<th>Concentration in $^{40}$Ar cylinder ($\mu$mol/mol)</th>
<th>Concentration in $^{36}$Ar cylinder ($\mu$mol/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{36}$Ar</td>
<td>81.9</td>
<td>balance</td>
</tr>
<tr>
<td>$^{38}$Ar</td>
<td>265.1</td>
<td>495.0</td>
</tr>
<tr>
<td>$^{40}$Ar</td>
<td>balance</td>
<td>13.2</td>
</tr>
<tr>
<td>Xe</td>
<td>44</td>
<td>0</td>
</tr>
</tbody>
</table>

### For reference R4:

When 100% nominal source gases are assumed: $R_{40/36} = 311.216$

### In reference R4:

$R_{40/36} = 303.494$

### In reference R5:

$R_{40/36} = 295.349$
### Expected uncertainty of reference mixture

<table>
<thead>
<tr>
<th>Factors</th>
<th>( u(R_{40/36}) )</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weighing (^{36}\text{Ar} )</td>
<td>0.061</td>
<td>0.03 mg uncertainty in weighing</td>
</tr>
<tr>
<td>(^{36}\text{Ar} ) in enriched (^{40}\text{Ar} )</td>
<td>0.014</td>
<td>Uncertainty of 0.002 in K36 assumed</td>
</tr>
<tr>
<td>(^{\text{Xe}} ) in enriched (^{40}\text{Ar} )</td>
<td>0.004</td>
<td>10 % uncertainty in (^{\text{Xe}} ) assumed</td>
</tr>
<tr>
<td>Total</td>
<td>0.063</td>
<td>Better than 5-fold from previous reference</td>
</tr>
</tbody>
</table>

Samples near “natural” composition will be measured using MAT 253 using the prepared reference in this work.

- This cannot measure all of the mass numbers.
- **Only recently it was configured to measure argon isotopes.**
- Much better repeatability than MAT 271.
- Limited linearity: only can be used near “natural” composition.

**Expected uncertainty in \( M_{\text{Ar}} \): \( 0.2 \times 10^{-6} \)
- We hope that using MAT 252 we can resolve \( R_{38/36} \) shift from the natural fractionation line, which added \( 0.35 \times 10^{-6} \) relative uncertainty in 2014 work.**
Helium isotopic reference gas at KRISS

- $^3\text{He}/^4\text{He}$ mass ratio is 0.75
- Sensitivity difference of $^3\text{He}$ and $^4\text{He}$ is larger: $K$ factor further away from 1
- Three isotopic reference mixtures were created:
  \[ R_{4/3} = 18.905 \pm 0.036, 98.78 \pm 0.21, 209.82 \pm 0.44 \]
- Helium isotopic concentration from different commercial sources will be investigated.

Things to be done and summary

• Finalize the analysis on both source gases and prepared reference R4 and R5.
• Validate the consistency between R4 and R5.
• Check the consistency with 2005 prepared references (R2 and R3).

• With new isotopic mixtures and enhanced MAT 253, KRISS will be able to provide molar mass of argon measurement with the relative uncertainty of $0.2 \times 10^{-6}$.
• With new helium isotope reference, KRISS can also provide traceable helium isotopic composition measurements.

• Thank you.