Effect of temperature gradient on calorimetric measurements during gas-loading experiments

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Abstract

We studied the influence of the temperature gradient on heat measurements during gas-loading experiments. The quasi isothermal chamber that we conducted our experiments in is built to keep the inside temperature uniform. However, when experimenting at the elevated temperatures above 200°C nonuniformities induced by the air flow inside the chamber produce local hot and cold spots.

The sample vessel inside the isothermal chamber went through pressurization/depressurization cycles to detect any temperature change due to gas-loading process. The presence of gas changes drastically the heat conduction inside the vessel. Therefore, when under pressure, the temperature probe couples to adjacent hot or cold spots more efficiently than when under vacuum. This coupling effect artificially shifts the measurement baseline up or down, which could be mistaken for excess heating or excess cooling.

We intentionally formed hot and cold spots by placing a resistor or Peltier element on the surface of the sample vessel that was later pressurized with hydrogen or helium. We observed both upward and downward temperature baseline shifts that were independent of gas type. In addition we used a heat sleeve that is sometimes used for gas-loading experiments at elevated temperatures. The heat sleeve also produced temperature baseline shift that in our system configuration resulted in 3% of apparent excess power production.

We conclude by emphasizing the importance of testing the measurement system with inert gas (preferably helium due to its similar value of thermal conduction coefficient to that of hydrogen) to eliminate the measurement error induced by temperature gradients.
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April 2012
Motivation (June 2011)

- Ni catalyst
- H$_2$ pressurization
- Cooling & heating observed
Motivation (February 2012)

• ZrO-Ni from Dr. Brian Ahern
• H₂ & D₂ pressurizations
• 50 mW excess power

390°C under 1200 torr

2 hours

H₂  H₂  H₂  D₂  D₂  D₂

H₂

50 mW

2nd hydrogen run (pressure 1200 torr)
signal at 390 °C
Motivation

• Excess heat generation:
  – at high temperatures (>250°C)
  – same for H₂ and D₂
  – no decline over time (4 days!)
  – depends on vessel location
Questions to answer

• What causes baseline shift?
• Can we enhance effect intentionally?
  – excess heat
  – excess cold
• Independent of gas type?
• Applicable to other gas-loading experiments?
Gas-loading system

- Precision of temperature control 10 mK
- 6g of material
- Pressure up to 1200 torr
- Chamber temperature 40 - 390°C
Thermal gradient in chamber
Hypothesis

1. Gas in

2. Increase thermal conductivity

3. Couple thermistor to local hot or cold spot

4. Measured baseline shifts

5. Gas out

6. Decrease thermal conductivity

7. Measured baseline shifts back

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Hot spot coupling

$T_1 < T_2 < T_3$

Gas convection

Thermocouples

Vacuum

Gas
Forming hot spot intentionally

- Hot spot: 150 Ohm resistor:
  - 1 watt
  - 4 watt
Effect of hot spot in the presence of gas

- For our configuration:
  - 0.90°C $\rightarrow$ 0.8 W
    - apparent excess heat 20%
  - 0.21°C $\rightarrow$ 0.17 W
    - apparent excess heat 17%

a) 4 W  
b) 1 W

0 W no resistor – no hot spot

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Independent of gas type

- Chamber at 100°C
- H₂, He 1200 torr
- Hot spot 1 watt
- H₂ and He runs show same exothermic shift of the baseline
- H₂ runs show spikes: loading/unloading in Ni
Cold spot coupling

Vacuum

Gas

Thermocouples

\[ T_2 > T_3 \]
Forming cold spot intentionally

- Peltier element - cooling
Forming cold spot intentionally

- For our configuration:
  $0.025^\circ C \rightarrow 0.013 \text{ W}$

  apparent excess cooling 1.6%
Creating hot spot by heat sleeve

For our configuration:

2°C  ->  1.2 W
Apparent excess heat 3%
Summary

- Temperature gradient causes measurement artifact
- Conditions were recreated by
  - Resistor – hot spot – baseline shifts upwards
  - Peltier elem. – cold spot – baseline shifts downwards
- Heat sleeve: apparent excess heat 3%
Conclusion

Inert gas must be used to rule out temperature measurements artifacts