

Research Article

Measurement Artifacts in Gas-loading Experiments

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Abstract

Numerous reports on gas loading of hydrogen isotope into powdered materials indicate excess heat generation that could be the result of a low energy nuclear reaction (LENR). When the amount of generated heat is small, it is important to characterize the calorimeter to account for possible measurement errors, or artifacts, which can result in long-term apparent excess heat. In this paper we investigate one of those possible measurement artifacts applicable to the gas loading systems that (1) use thermometry as a proxy for energy flow measurements, and (2) run at elevated temperatures. When loading gas into Pd-impregnated alumina, we have found that thermal gradients inside the system result in apparent heating or cooling of the measuring system. We experimentally magnified this effect and confirmed that it was due to temperature nonuniformity inside the calorimetric system. We quantified the effect using a numerical simulation tool to show that a temperature gradient as small as 0.5 K/m might result in 50 mW of apparent excess heat “generation”. We suggest a simple approach for investigators to account for this measurement artifact by calibrating their systems with helium gas either prior to, or at the end of, the experimental sequence.

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1. Introduction

In recent years investigations have been reported on deuterium and hydrogen gas loading of a variety of nanoparticle materials including Pd- and Ni-based composites [1–6] because they have exhibited anomalous heat production and can potentially be used in the energy-generating devices. Excess heat observed in these systems is interpreted as an evidence of a low energy nuclear reaction (LENR). In the absence of reproducible data on nuclear byproducts, the majority of the reports are based on heat measurement results. The systems used for these experiments has varied but the basic concept of comparing the amount of heat generated by the system in the presence or in the absence of the reacting gas is common to all experiments.

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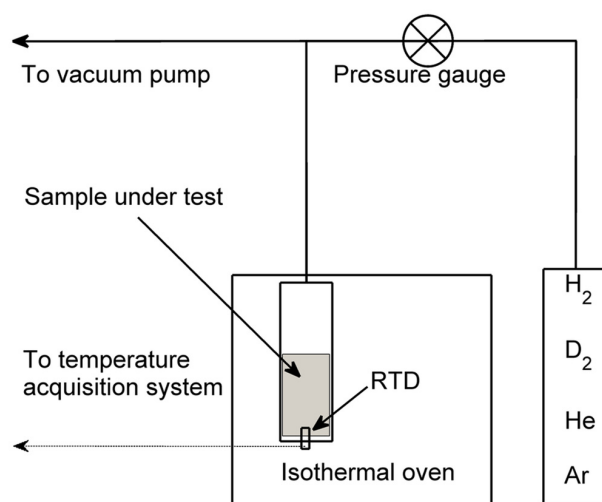


Figure 1. Schematic representation of the gas-loading system. The sample vessel is enclosed in an oven. Temperature is measured using resistance temperature detectors (RTDs).

We have replicated and analyzed the results of gas-loading reactions in Pd and Pt-impregnated alumina and zeolite powders and Pd-coated Ni-based composites. Earlier studies showed that some excess heat could be explained by the chemical reaction of substituting hydrogen with deuterium in residual water trapped in the material, known as an H/D exchange reaction [5,6]. However, at temperatures above 200°C we observed heating and cooling that could not be explained by conventional chemistry. Anomalous temperature shifts were observed as long as the sample was under gas pressure, with the longest run lasting 96 h, after which the sample was evacuated and the gas was removed. This run was performed at 390°C, and 50 mW of estimated excess heat was observed. The effect went away when the vessel was repositioned inside the experimental chamber, which gave rise to the question as to whether a measurement artifact could account for these observations. While we discovered this artifact in our setup, it is possible that any other gas loading system which uses thermometry to evaluate energy flow could be a subject to this error. Experiments that are run at elevated temperatures are more prone to this artifact since the temperature gradients are naturally higher. In this paper we describe our investigation of this measurement artifact and conclude by suggesting the calibration technique that can account for it.

2. Experiment

2.1. Experimental system and procedure

Figure 1 shows the block diagram of the experimental setup. The vacuum system was enclosed in an isothermal chamber (an HP 5890A gas chromatograph oven). This oven is designed for precise temperature control. The temperature uniformity across the oven is achieved by constant air flow produced by a heater and a fan at the back panel of the oven. The temperature of the oven can be set anywhere between 40°C and 400°C. We ran all the experiments at temperatures below 390°C.

Removable stainless steel vessels, which are part of the vacuum system, were placed inside the oven and connected to the gas line. Pipe plug resistance temperature detectors (RTDs) (Omega p/n RTD-NPT-72-E-MTP-HT) were welded

into the bottom of the vessels to measure temperature change. The sample material was loaded into the vessels.

Hydrogen, deuterium, helium, or argon were supplied through the gas line. The vacuum system was pressurized up to 1.6×10^5 Pa (1200 torr). A turbo-molecular pump was used to evacuate the system down to 10^{-5} Pa. System control, and temperature and pressure data acquisition were carried out with LabView software.

A typical run consisted of (1) pressurization by a gas of choice, (2) a period of time when the vacuum system remained under gas pressure, and (3) an evacuation step. Heat production or consumption was determined from temperature changes in the vessel, whose transient temperature can deviate from the constant oven temperature baseline. Net positive temperature change measured using the RTD was considered as heating, and negative as cooling.

2.2. Material

For this study we used three samples: alumina powder with no Pd content (Fisher Scientific P/N: CAS 1344-28-1), 2% by weight Pd-impregnated alumina powder, and commercially available Ni powder (Alfa Aesar P/N 43214). We tested these materials to see how their thermal conductivity affected the measurements. The chemistry and fabrication method of wet impregnation of Pd metal into alumina are beyond the scope of this paper, and a detailed description can be found in Ref. [6].

2.3. Hypothesis

We conducted our experiments in an isothermal oven. The sample vessel inside the oven then went through gas pressurization/depressurization cycles to detect a temperature change due to the gas-loading process. The assumption in gas-loading experiments is that heat produced under gas pressure is an indication of a reaction inside the vessel. This is a valid assumption as long as a stable temperature baseline is established, and temperature is uniform across the oven. However, at elevated temperature this uniformity is broken due to location-dependent variations in hot air flow from the oven heater. The effect becomes more noticeable as the temperature setting is raised. Local hot and cold spots are created as a result of this nonuniformity. Because the stainless steel vessel is a poor heat conductor when it is evacuated, such hot and cold spots couple weakly to the RTD. However, when the vessel is pressurized, the presence of gas changes drastically the heat conduction inside it and causes the RTD to couple more efficiently to the hot or cold spots in the oven than when under vacuum. This results in channeling of heat from or into the oven environment. This channeling effect can artificially shift the measurement baseline up or down, which can be mistaken for anomalous heating or anomalous cooling.

To test this hypothesis we artificially created and enhanced the hot and cold spot effect by placing a local heating or cooling element on the surface of the vessel that would later be pressurized with hydrogen, deuterium, helium, or argon. If our hypothesis is correct, then in the presence of the hot spot (dissipative resistor), the measurement baseline would shift upwards when the vacuum system was pressurized, and in the presence of the cold spot (Peltier element), downwards. Moreover, the difference in the heat conduction coefficients of supplied gases should affect the magnitude of the baseline shift. While hydrogen, deuterium and helium have similar thermal conduction coefficients, argon's thermal conductivity is ten times smaller. If our assumption is correct than an argon run would show a smaller baseline shift. The presence of material inside the vessel should also affect the conductive characteristics of the vacuum system, and thus the magnitude of a baseline shift. When evacuated, a loose powdered material is a poor heat conductor due to the spacing between the particles. When under pressure, however, the gas might establish a thermally conductive channel between particles. We expected the effect to be a result of a mixed contribution of the different factors such as the powder's packing density and the thermal conductivity of the sample.

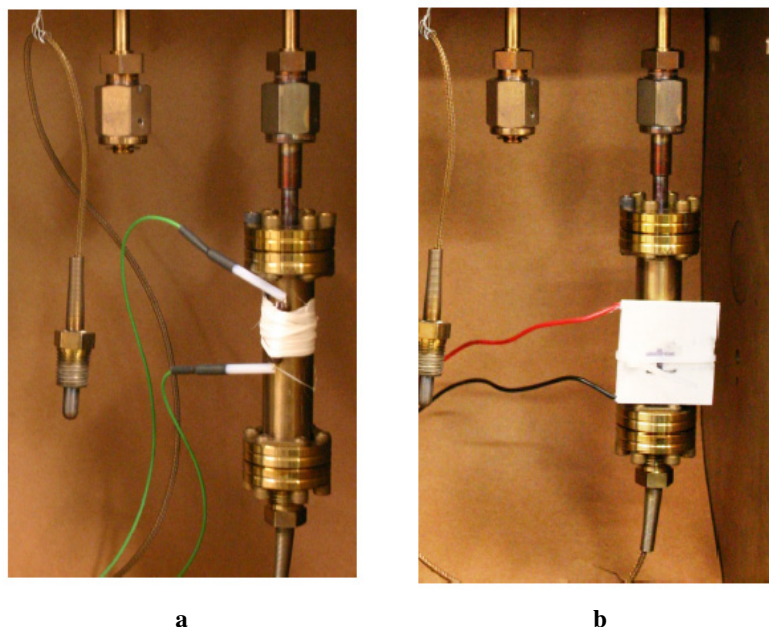


Figure 2. The vessel inside the oven with a (a) dissipative resistor, (b) cooling element.

3. Results

3.1. Hot spot

The hot spot was formed by placing a $150\ \Omega$ resistor on the surface of the vessel, containing 6 g of Pd-impregnated alumina powder. Figure 2 (a) shows the view inside the oven, with the resistor attached on the surface of the vessel.

The oven was kept at 100°C , and 1 W was dissipated in the resistor. The purpose of this exercise was to simply create a thermal gradient across the vessel. In Fig. 3 plot (a) shows the results of the gas pressurizations carried out in the absence of an artificially created thermal gradient.

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When no power was dissipated through the resistor the only temperature changes during pressurization cycles were due to absorption/desorption of the hydrogen isotopes in Pd [7] and the gas compression/expansion. Since neither helium nor argon is absorbed in Pd, the runs with those gases showed only temperature change associated with gas compression/expansion. The picture changes drastically when we powered the resistor. In Fig. 3, plot (b) shows a visible baseline shift whenever the vacuum system was pressurized. The baseline shift was similar for deuterium, hydrogen and helium runs and different for argon.

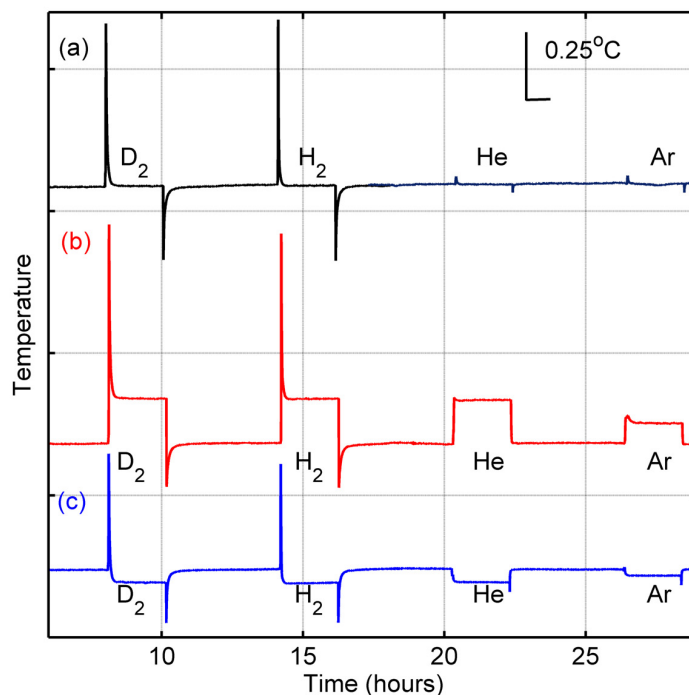


Figure 3. Experimentally observed temperature changes due to gas loading of Pd-impregnated alumina (a) in the absence of an artificially produced thermal gradient; (b) in the presence of a hot spot; (c) in the presence of a cold spot. Pressurizations were carried out with deuterium, hydrogen, helium and argon.

3.2. Cold spot

The cold spot was formed by a Peltier element (TEC1-12706) held against the vessel surface as shown in Fig. 2 (b). The oven temperature was set to 40°C and 0.1 W was dissipated through the Peltier element. We cycled hydrogen, deuterium, helium and argon through the vacuum system inside the oven, while having the Peltier element constantly on. The results are shown in Fig. 3, plot (c). Each pressurization resulted in the downward shift of the temperature baseline. The magnitude of the shift depended on the gas used in the experiment.

4. Numerical simulations

In order to quantify the measurement artifact caused by the temperature gradient inside the oven we used COMSOL commercial software to simulate heat conduction in the vessel. We interpolated the hot spot experimental data to evaluate the magnitude of a temperature nonuniformity that could cause the 50 mW baseline shift discussed in the Introduction. Figure 4 shows the result of the COMSOL simulation. In the solver the temperature of the surroundings was set to 390°C (663 K). A heating stripe at 390.084°C was simulated on the vessel's surface. Due to heat transfer and losses, the probe at the bottom of the vessel would read 390.060°C. Based on the simulations, a 0.5 K/m temperature gradient would result in 50 mW of apparent heating under the gas pressure. This noticeable effect was produced by

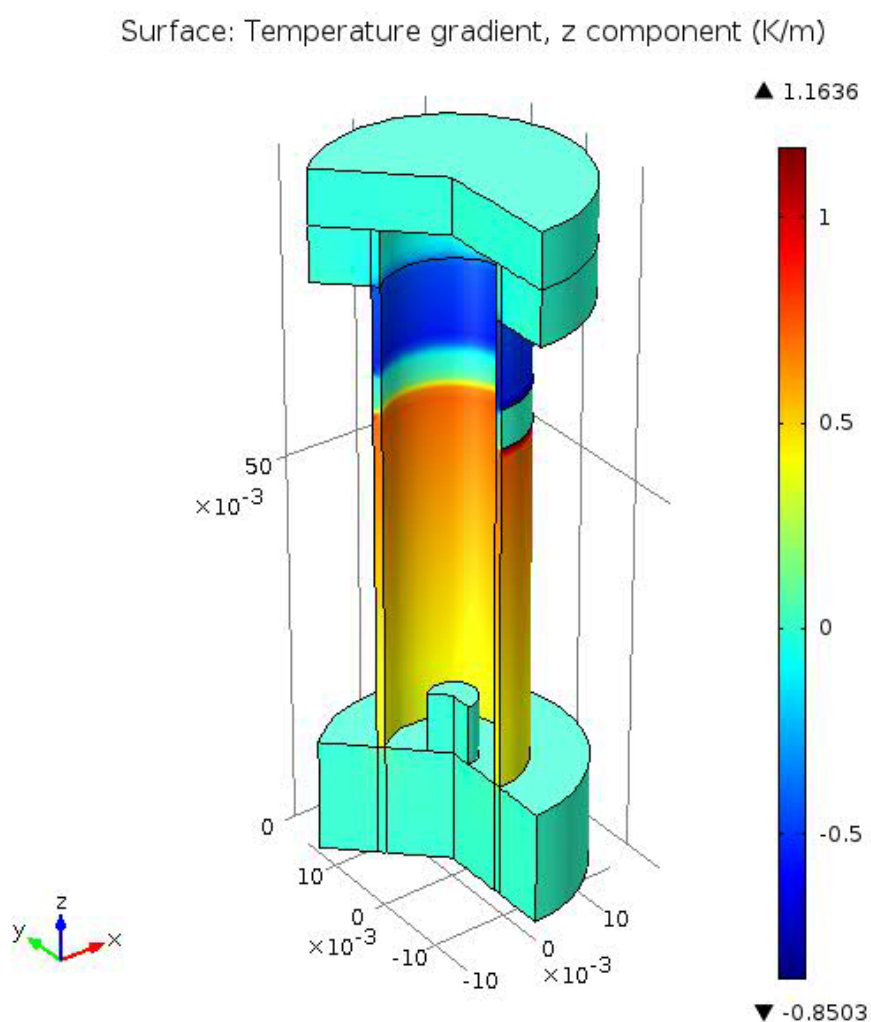


Figure 4. COMSOL simulation of the temperature gradient in the stainless steel vessel as a result of the local heating around the neck of the vessel. In this particular notation the temperature gradient is positive towards the bottom of the vessel. The portion of the vessel above the heating rings conducts heat as well, but the gradient is in the opposite direction, represented by the negative value.

relatively small temperature gradient of 0.024°C along the 4.5 cm long vessel wall. The purpose of this simulation was to show that relatively small temperature nonuniformity inside the experimental chamber would result in observable apparent heating by the temperature sensor.

5. Discussion

We enhanced the effect of the temperature gradient in order to study its ramification on the temperature measurements. Placing a resistor on the surface of the vessel formed a hot spot. The addition of gas to a previously evacuated system increased the thermal conductivity of the vessel and allowed better coupling to the local hot spot (resistor). As a result the measured temperature baseline shifted up. When the gas was removed, the coupling weakened due to the conductivity decline, and the temperature baseline shifted back to its initial position. We used a cooling Peltier element to confirm the downward baseline shift. Quantitative analysis of particular case of apparent heating was simulated using COMSOL Multiphysics.

The magnitude of the shift depended on (1) the magnitude of the thermal gradient, (2) the thermal conductivity of the gas, (3) the presence of material inside the vessel.

- (1) Increasing the local hot spot temperature resulted in an increased amount of heat available for channeling from/to the oven's environment (and opposite for the cold spot), affecting the magnitude of the baseline shift. We confirmed this hypothesis by dissipating different amount of power in the resistor. Doubling the power resulted in a doubling of the temperature baseline shift.
- (2) Gases of higher thermal conductivity (hydrogen, deuterium and helium) showed greater temperature baseline shifts, as compared to less-conductive argon. However, the trend was qualitative than quantitative. Even though argon's conduction coefficient is ten times smaller than that of helium, the baseline shift was only a factor of two smaller. We interpreted this as a mixed contribution of conductive and convective heat transfer mechanisms.
- (3) The presence of a sample inside the vessel resulted in a larger baseline shift as compared to the shift observed from gas loading in an empty vessel (results not shown). Three different materials were tested: Pd-impregnated alumina, un-impregnated alumina and Ni powder. Ni is three times more thermally conductive than alumina, but a simple proportionality between the thermal conductivity of the materials and the magnitude of the baseline shift was not observed (results not shown). We suggest that some other material properties (e.g., powder density) also affected the heat conduction process.

6. Conclusions

We studied the influence of the temperature gradient on heat measurements during gas-loading experiments. To clearly demonstrate the observed effect we enhanced the temperature gradient by placing a heating or cooling element on the surface of the sample vessel and later pressurized it either with hydrogen, deuterium, helium, or argon. We observed both upward and downward temperature baseline shifts. The magnitude of the shift depended on the magnitude of the temperature gradient and the thermal conductivity of the gas inside the vessel. While we discovered this artifact in our quasi-isothermal oven, the results are applicable to any other gas loading system that uses thermometry to evaluate energy release/consumption. Moreover, the experiments that are run at the elevated temperatures are more prone to this artifact since the temperature gradients are naturally larger.

We quantified the effect by simulating heat conduction inside the sample vessel using finite element software. According to the simulations at 390°C, the effect would become visible with a diminutive 0.024°C temperature difference along the 4.5 cm long vessel wall, and result in 50 mW of apparent heating.

We conclude by emphasizing the importance of testing the measurement system with the material pressurized by helium gas, which has a thermal conductivity similar to hydrogen and deuterium, to identify potential measurement artifacts caused by temperature gradient.

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