Metal hydride differential scanning calorimetry as an approach to compositional determination of mixtures of hydrogen isotopologues and helium

David B. Robinson[*], *Weifang Luo, Trevor Y. Cai, Kenneth D. Stewart*

Sandia National Laboratories, PO Box 969 MS 9291, Livermore, CA, USA

ARTICLE INFO

ABSTRACT

Gaseous mixtures of diatomic hydrogen isotopologues and helium are often encountered in the nuclear energy industry and in analytical chemistry. Compositions of stored mixtures can vary due to interactions with storage and handling materials. When tritium is present, it decays to form ions and helium-3, both of which can lead to further compositional variation. Monitoring of composition is typically achieved by mass spectrometry, a method that is bulky and energy-intensive. Mass spectrometers disperse sample material through vacuum pumps, which is especially troublesome if tritium is present. Our ultimate goal is to create a compact, fast, low-power sensor that can determine composition with minimal gas consumption and waste generation, as a complement to mass spectrometry that can be instantiated more widely. We propose calorimetry of metal hydrides as an approach to this, due to the strong isotope effect on gas absorption, and demonstrate the sensitivity of measured heat flow to atomic composition of the gas. Peak shifts are discernible when mole fractions change by at least 1%. A mass flow restriction results in a unique dependence of the measurement on helium concentration. A mathematical model is presented as a first step toward prediction of the peak shapes and positions. The model includes a useful method to compute estimates of phase diagrams for palladium in the presence of arbitrary mixtures of hydrogen isotopologues. We expect that this approach can be used to deduce unknown atomic compositions from measured calorimetric data over a useful range of partial pressures of each component.

Introduction

The heavier isotopes of hydrogen are important in the operation of nuclear reactors, in studies of nuclear fusion, and in analytical methods such as gas chromatography and nuclear magnetic resonance spectrometry. In heavy-water reactors, presence of ^1H degrades reactor performance, and presence of radioactive ^3H is a safety hazard. Efforts are made to purify isotopic mixtures through water distillation, water electrolysis, methods based on absorption or adsorption, and hybrids of these. Hydrogen—helium mixtures result when ^3H decays to ^3He. Mixtures of $^1H_2$ and ^4He may be generated during gas chromatography if the carrier gas is varied. The increasing

---

cost of helium is prompting recycling efforts, where characterization of mixture composition would be useful. Mixtures can also be generated during synthesis or reclamation of isotopically labeled organic compounds that are useful in nuclear magnetic resonance spectrometry.

Currently, mass spectrometry is the main method to determine the composition of gaseous mixtures of hydrogen isotopologues and helium [1,2]. Mass spectrometers are bulky, expensive, and energy intensive, and they require vacuum maintenance. This is especially onerous when tritium is used, requiring handling of dilute radioactive pump exhaust, and periodic disposal of worn out pump components that have radioactive contamination. Some commercial quadrupole mass spectrometers have difficulty distinguishing species of similar mass such as $^2H_2$ and ^4He, or the diatomic molecule $^1H^2H$ and ^3He. Finite filter bandwidths, and generation of minor species such as H_3^+, limit the ability to measure trace species in a mixture.

If composition could be measured by a method that is more compact and lower power, without consuming or dispersing the sampled gas, it will be possible for a gas handling system to report composition at more sampling points, allowing deviations from target values to be corrected before they propagate to other parts of the system, improving system reliability and safety, and improving efficiency of gas use.

Calorimetry is an experimental technique that has been successfully miniaturized in the form of sub-millimeter, sub-milliwatt sensors [3—5]. We desire to adopt this method for use in processes involving the hydrogen isotopologues and helium. With a compact sensor for these gases, the composition of process gases can be known and controlled at a larger number of points throughout a system, improving reliability of process operations, without incurring the cost of bulky component disposal after replacement. In this report, we focus on study of milligram-scale palladium samples in the presence of varying gas mixtures using a commercial differential scanning calorimeter. This has allowed us to determine the basic chemical and physical sensing characteristics. For hydrogen detection, we rely on the sensitive isotopic dependence of the temperatures of hydrogen absorption and desorption by palladium. This dependence is primarily on atomic composition, and does not easily reveal how the gas-phase isotopes are arranged as diatomic isotopologues, but the atomic composition is still useful information. The approach can resolve mixtures of two different isotopes, but not all three; we focus on ^1H and ^2H here. To determine the amount of helium, we rely on its mass transport effects in the presence of a flow restriction. A satisfactory model of the system is constructed using simple assumptions about mass transport and the metal hydride phase behavior. In principle, this model could be used to determine previously unknown atomic compositions from experimental data, which would be necessary for the development of a practical sensor.

Scanning calorimetry in hydrogen atmospheres has proven to be a valuable technique in the study of solid-phase hydrides and deuterides such as those of palladium [6,7], palladium alloys [8,9], magnesium alloys and compounds [10—12], and lanthanum alloys [13], so there is precedent for our experimental methods. The behavior of metal hydrides in mixtures of hydrogen isotopologues [14—17] and inert gases [18] has also been studied. This prior work adds confidence that our proposed approach can be understood in detail. A significant body of prior knowledge of palladium hydride thermochemistry [19] and the demonstration of the high reversibility of palladium to hydriding and dehydriding cycles [20] motivated our choice of palladium as a sorbent material in this work.

Materials and methods

The commercial calorimeter used is the Mettler Toledo HP DSC 1, which is essentially a differential scanning calorimeter mounted inside a pressure vessel. The instrument comes with a mass flow control module that was bypassed for our studies. The palladium (Pd) powder was purchased from Engelhard, and has a surface area of about 1 m^2/g. This corresponds to a particle size of about 0.3 μm, assuming the particles are spheres. A sample of about 10 mg Pd powder is placed in a 40-μL aluminum pan, and a lid with a 50 μm diameter laser-drilled hole is crimped onto the pan to form a capsule. The Pd mass for the data presented here is 11.1 mg. An empty capsule with a similar hole is used as a reference. These capsules are placed side by side on a heater-thermocouple assembly that is mounted in the pressure vessel, which has an operating range from 0 (vacuum) to 10 MPa. As a cleaning procedure, an air-exposed Pd sample is heated to 150 °C and cycled 3 times between vacuum and several tens of kPa H_2 prior to any calorimetry experiments.

The instrument was calibrated by performing calorimetry experiments with a capsule containing about 6 mg indium in the presence of helium. The instrument software uses the known melting point and enthalpy of indium to determine the temperature and heat flow scales. A time lag correction that partially compensates for the finite response time of the system is also made by performing this calibration at several scan rates.

A homemade gas manifold was fabricated to deliver gas to the pressure vessel. The manifold allows argon, hydrogen, gas from an auxiliary port, and vacuum to be applied to the pressure vessel. Vacuum is provided by a rotary vane pump. The auxiliary gas is typically helium or deuterium in a 1-L pressure vessel at 200 psi, with its own regulator. The manifold is equipped with a 100 psi pressure transducer, 90 psi pressure relief valve, and a vacuum gauge that measures to the millitorr range. Pneumatic valves and interlocked switches control gas flow on the front panel. The auxiliary gas port is controlled through a manual valve. The argon is used only to fill the chamber prior to opening it to change samples. Gas mixtures were prepared by dosing a given pressure of a first gas to the chamber, followed by a dose of a second gas to the desired total pressure, and then waiting at least 30 min for gases to mix. Experiments performed after this amount of time give essentially the same result as experiments performed with longer mixing times.

We refer interchangeably to ^1H and H, and ^2H and D (deuterium). However, T refers to absolute temperature, and not tritium.